PYROLYSIS OF 1-METHYL-2-PHENYLDIAZENE

ARTHUR M. COOK

PYROLYSIS OF 1-METHYL-2-PHENYLDIAZENE

by

© Arthur M. Cook, B.Sc.

Submitted in partial fulfillment of
the requirements for the degree of
Master of Science

Department of Chemistry
Memorial University of Newfoundland
St. John's, Newfoundland, Canada
A1B 3X7

July, 1988

ISBN 0-315-50464-1

Abstract

The question of whether diazenes lose nitrogen through one or two bond scission has been a subject of study for over fifty years. Using recently available data on azobenzene and previously published Arrhenius parameters for azomethane a kinetic approach was taken to this problem using 1-methyl-2-phenyldiazene.

In the first part of this thesis the synthesis and purification of 1-methyl-2-phenyldiazene is described.

The next section deals with the construction of the vacuum line and its associated apparatus. The problems with the original design are discussed and modifications which were made to the line are outlined.

In the results section are presented the definition of the rate constant for nitrogen formation and a table of products of reaction, which, with the associated appendices show how the products were identified and measured. The yield-time, order, and Arrhenius plots are then presented for both the unpacked and packed reaction vessels as well as results for experiments in which propene was present.

A summary of the observations is first given in the discussion section. The possibility of direct decomposition of 1-methyl-2-phenyldiazene with no contribution from the chain is next discussed, along with a consideration of the *trans* to *cis* isomerization. Both are shown to be implausible, using aguments based on the results obtained.

Based on the effect of propene, the orders of reaction, and the values of the Arrhenius parameters, two mechanisms are then proposed. The simple one is written to show that nitrogen may be formed by a chain reaction as well as by simple fission of 1-methyl-2-phenyldiazene. It is solved to show that it is first order with respect to nitrogen formation. The second mechanism accounts for the products of reaction, and also adds a second chain to the pyrolysis. Speculation on the formation and

reaction of diradicals is then made. The complete mechanism is then solved to show that it too is first order with respect to nitrogen formation.

Possible Arrhenius parameters of the simple fission of 1-methyl-2-phenyldiazene are then proposed based on the propene results. These parameters agree quite well with what Forst and Rice obtained for azomethane and suggest one bond scission of 1-methyl-2-phenyldiazene.

Speculation as to why, in the initial series of propene experiments, no inhibition of the rate of nitrogen formation appeared is then made. The possible role of phenylhydrazone* is also considered.

Finally, the erratic behavior of the reaction after the initial series of propene experiments is commented on, and further directions for the study of this reaction are presented.

---

* phenylhydrazone of methanal

Acknowledgements

I first of all wish to express my gratitude to my supervisor, Dr. Don Barton, for kindling my interest in gas phase kinetics and for his advice and encouragement during the course of this work.

I am indebted to the staff of Memorial University's Technical Services Department for their expertise and technical assistance with apparatus and equipment. I would particularly wish to thank glassblowers Mr. Doug Seymour, Mr. Martin Hatswell and Mr. Tom Perks.

The assistance and helpful advice of Mr. Avery Earle in performing the linear regression analysis and preparation of the associated figures was also greatly appreciated.

The encouragement of Dr. Peter Golding throughout this project, along with the use of his lab and equipment is gratefully acknowledged.

I also wish to thank Miss Teresa Barker for typing this thesis and Mr. John Kane for preparation of the figures.

Finally I wish to thank Dr. Keith Winter and the Division of Junior Studies, and the Department of Chemistry, for financial support during the course of this study.

Table of Contents

	Page
Abstract	ii
Acknowledgements	iv
List of Tables	vii
List of Figures	ix
I. Introduction	1
II. Experimental	8
1. Preparation of 1-Methyl-2-Phenyldiazene and Purification of Propene	8
a. Synthesis	8
b. Purification of Batch A	9
c. Purification of Batch B	10
d. Purification of Propene	13
2. Vacuum Line	14
a. Pumping System	14
b. Toepler Pumps	14
c. Pressure Gauge	20
d. Reaction Vessels	20
e. Reaction Vessel Oven	20
f. Gas Chromatograph	22
g. Air Bath	23
3. Procedure	27
a. Packed Reaction Vessel	27
b. Unpacked Reaction Vessel	28
c. Unpacked Reaction Vessel and Propene	28
III. Results	29
1. Definition of Rate Constant	29
2. Unpacked Vessel	29
a. Products	29

b. Yield versus Time Plots 30
c. Order Plots 32
d. Addition of Propene 32
e. Rate Constant *versus* Temperature and Arrhenius Plot 45
3. Packed Vessel 45
IV. Discussion 55
1. Interpretation of Data 55
2. Rate Controlling Elementary Fission 55
3. Rate Controlling Isomerization 56
4. Chain Reaction 56
a. Simple Mechanism 56
b. Simple Mechanism with R_1, R_2 Termination 60
c. Complete Mechanism 62
d. Speculation on the Formation and Reaction of Diradicals . . . 66
i) Addition 67
ii) Insertion 68
e. Rate Equation for the Complete Mechanism 68
5. Comments on the Results with Propene 75
6. Speculation on the Effect of Storage 76
7. Speculation on the Role of Phenylhydrazone 76
8. Comments on Erratic Behavior of Rate of Reaction 77
9. Summary and Suggestions for Future Research 78
References 80
Appendix A 83
Appendix B 85
Appendix C 116
Appendix D 158

List of Tables

		Page
Table 1.	Products and mole percent for a sample run at 559.05 K.	31
Table 2.	Yield *versus* time data for nitrogen and methane at 559.0 K in unpacked vessel with calculated slopes and intercepts.	35
Table 3.	Yield *versus* time data for nitrogen and methane at 529.4 K in unpacked vessel with calculated slopes and intercepts.	36
Table 4.	Data for the order plots of nitrogen and methane at 559.0 K in unpacked vessel with calculated slopes.	39
Table 5.	Data for the order plots of nitrogen and methane at 529.4 K in unpacked vessel with calculated slopes.	40
Table 6.	Data for the order plots of nitrogen and methane at 559.0 K with propene added in unpacked vessel and the calculated slopes.	42
Table 7.	Examples of normal and erratic runs at 529.4 K without propene	46
Table 8.	Data for the exponential fit of the rate of nitrogen formation *versus* temperature with the calculated activation energy and pre-exponential factor in unpacked reaction vessel.	47
Table 9.	Data for the exponential fit of the rate of nitrogen formation *versus* temperature with the calculated activation energy and pre-exponential factor in packed reaction vessel.	53
Table 10.	Mean rate constant for nitrogen formation in the packed and unpacked reaction vessels.	54
Table 11.	High resolution mass spectra of starting material for kinetic experiments.	84
Table 12.	Mass spectra of scan number 104 of 1-methyl-2-phenyldiazene from spinning band column.	90
Table 13.	Mass spectra of scan number 207 of 1-methyl-2-phenyldiazene from spinning band column.	91
Table 14.	Mass spectra of scan number 504 of 1-methyl-2-phenyldiazene from spinning band column.	92
Table 15.	Mass spectra of scan number 918 of 1-methyl-2-phenyldiazene from spinning band column.	93
Table 16.	Mass spectra of scan number 299 of 1-methyl-2-phenyldiazene	

from spinning band column. 94

Table 17. Mass spectra of scan number 940 of starting material. 97

Table 18. Mass spectra of scan number 98 of starting material. 98

Table 19. Mass spectra of scan number 214 of starting material. 99

Table 20. Mass spectra of scan number 510 of starting material. 100

Table 21. Mass spectra of scan number 89 of condensed fraction. 103

Table 22. Mass spectra of scan number 107 of condensed fraction. 104

Table 23. Mass spectra of scan number 124 of condensed fraction. 105

Table 24. Mass spectra of scan number 129 of condensed fraction. 106

Table 25. Mass spectra of scan number 432 of condensed fraction. 107

Table 26. Mass spectra of scan number 443 of condensed fraction. 108

Table 27. Mass spectra of scan number 469 of condensed fraction. 109

Table 28. Mass spectra of scan number 506 of condensed fraction. 110

Table 29. Mass spectra of scan number 936 of condensed fraction. 111

Table 30. Mass spectra of scan number 1515 of condensed fraction. 112

Table 31. Mass spectra of scan number 212 of condensed fraction. 113

Table 32. Mass spectra of scan number 275 of condensed fraction. 114

Table 33. Mass spectra of scan number 306 of condensed fraction. 115

List of Figures

		Page
Figure 1.	Collection apparatus for column effluent.	12
Figure 2.	Schematic of initial vacuum line.	16
Figure 3.	Schematic of Toepler pumps.	18
Figure 4.	Schematic of switching valves on vacuum line and gas chromatograph.	19
Figure 5.	Schematic of reaction vessel oven.	21
Figure 6.	Schematic of redesigned vacuum line.	25
Figure 7.	Yield *versus* time plots for nitrogen and methane at 559.0 K in unpacked reaction vessel.	33
Figure 8.	Yield *versus* time plots for nitrogen and methane at 529.4 K in unpacked reaction vessel.	34
Figure 9.	Order plot for nitrogen and methane at 559.0 K in unpacked reaction vessel.	37
Figure 10.	Order plot for nitrogen and methane at 529.4 K in unpacked reaction vessel.	38
Figure 11.	Order plot for nitrogen and methane at 559.0 K in unpacked reaction vessel with propene added.	41
Figure 12.	Plot of the rate constant for nitrogen formation *versus* initial ratio of 1-methyl-2-phenyldiazene to propene at 559.0 K in unpacked reaction vessel.	44
Figure 13.	Plot of the rate constant for nitrogen formation *versus* temperature in unpacked reaction vessel.	48
Figure 14.	Arrhenius plot for nitrogen in unpacked reaction vessel.	49
Figure 15.	Plot of the rate constant for nitrogen formation *versus* temperature in packed reaction vessel.	51
Figure 16.	Arrhenius plot for nitrogen in packed reaction vessel.	52
Figure 17.	Total ion current of the effluent from the gas chromatograph of the 1-methyl-2-phenyldiazene from the spinning band column.	89
Figure 18.	Total ion current of the effluent from the gas chromatograph of the starting material.	96
Figure 19.	Total ion current of the effluent from the gas chromatograph of the consolidated condensed fraction.	102

I Introduction

Rationale for this Research

Diazenes may pyrolyze by breaking two bonds simultaneously,

[1] $R-N=N-R \rightarrow 2R\cdot + N_2$

or, by breaking two bonds in sequence,

[1A] $R-N=N-R \rightarrow R-N=N\cdot + R\cdot$

[1B] $R-N=N\cdot \rightarrow R\cdot + N_2$

The subject, of one or two bond scission of diazenes, was raised in 1929 by Ramsperger (1). In his search for systems which could be used to test new theories of unimolecular reactions he pyrolyzed 1-methyl-2-isopropyldiazene and compared the activation energy of this reaction with those of azomethane and azoisopropane which he had previously studied. He found that the activation energy for the mixed diazene was between the other two values, and therefore concluded that there was two bond scission.

However, the rate measurements were made by monitoring pressure change because at that time the complexity of the stoichiometry was not realized and the difficulty of measuring elementary rate constants was not appreciated. When the elementary rate constants for nitrogen formation from azoisopropane (2) and azomethane (3) were eventually measured the values did not support Ramsperger's results, and so the comparison was invalid. Apparently 1-methyl-2-isopropyldiazene has not been studied subsequently.

In a recent study (4) of azobenzene pyrolysis, the elementary rate constant for nitrogen formation was reported. This result, along with Forst's (5) results for azomethane led to the suggestion of a comparison*, similar to Ramsperger's, of azomethane, azobenzene, and 1-methyl-2-phenyldiazene.

Azobenzene

A review of azobenzene pyrolysis in the gas phase shows that only two studies have been completed. In one, referred to above, reference (4), Arrhenius parameters for nitrogen formation were reported to be $10^{16.6}$ s^{-1} for the preexponential factor and 278 kJ mol^{-1} for the activation energy. In the other, Leiba and Oref (8) gave $10^{12.61}$ and 223 kJ mol^{-1}. The discrepancy seems to be due to problems of stoichiometry and treatment of data in the latter study. A discussion of the discrepancy is found in reference (4).

Azomethane

Since the publication of Ramsperger's pioneering work a number of studies have helped to determine the features of azomethane pyrolysis. The most important results are now reviewed.†

(1) Steel and Trotman-Dickenson (6) measured the rate of nitrogen formation and showed that it was inhibited by the addition of propene. They deduced from these results that a short chain was present in azomethane pyrolysis.

(2) Forst and Rice (5) next showed that addition of nitric oxide reduced the initial rate of nitrogen formation to a minimum value relative to that observed for the

---

* Since this project was started a mixed alkyl aryl diazene pyrolysis in the gas phase has been investigated (28). The Arrhenius parameters obtained for 1-ethyl-2-phenyldiazene in a stirred flow system using cyclohexene as a carrier gas were 209 kJ/mole for the activation energy and $10^{15.8}$ for the pre-exponential factor. The question to be asked of this study is: Does the use of cyclohexene as an inhibitor give the elementary rate constant? For comments, refer to the Discussion section.

† Those in which the progress of the reaction was monitored manometrically are omitted.

uninhibited reaction. Because catalysis as well as inhibition was observed the rate constant was calculated by extrapolating the rate back to zero nitric oxide pressure. The initial rates so calculated gave Arrhenius parameters of $10^{17.3}$ s^{-1} for the pre-exponential factor and 232 kJ mol^{-1} for the activation energy.††

(3) Forst and Paquin (7) carried out a comprehensive study of the products, and their rates of formation, for azomethane pyrolysis. A short chain mechanism was proposed, the main feature of which was chain propagation and nitrogen formation by decomposition of the radical CH_3-N=N-CH_2·.

(4) Two reports appeared in the literature (13,14) in which the Arrhenius parameters* differ markedly from those reported in reference (5). Both of these studies involved the azomethane sensitized decomposition of hydrocarbons, in which the rates of azomethane decomposition are extracted from rates of formation of products of hydrocarbon pyrolysis. In the interpretation of the results of the azomethane sensitized decomposition of isobutane a small molecular contribution to nitrogen production is considered,

$$CH_3 - N = N - CH_3 \rightarrow N_2 + C_2H_6.$$

(5) Benson (15) estimated the enthalpy of formation of azomethane by using thermodynamic group additivity. The enthalpy change for reaction [2], below, was then obtained. By assuming that the

---

†† A similar study of $CD_3N_2CD_3$ by D.-R. Chang and O.K. Rice (Int. J. Chem. Kinet. I. 171 (1969)) resulted in a slightly lower pre-exponential factor.

* The reported values of pre-exponential factors, A, and activation energies, E, in hydrocarbons for the reaction $CH_3N_2CH_3 \rightarrow N_2 + CH_3$ are listed.

	A	E
ethane	$10^{14.38}$ s^{-1}	199.2 kJ mol^{-1}
propane	$10^{14.78}$ s^{-1}	202.1 kJ mol^{-1}
isobutane	$10^{13.90}$ s^{-1}	193.6 kJ mol^{-1}

$$CH_3 - N = N - CH_3 \rightarrow 2CH_3\cdot + N_2 \qquad [2]$$

activation energy for nitrogen formation in the inhibited pyrolysis of azomethane was equal to the enthalpy change of reaction [2A] and [2B] he calculated the second

$$CH_3 - N' = \dot{N} - CH_3 \rightarrow CH_3 - N = N\cdot + CH_3\cdot \qquad [2A]$$

$$CH_3 - N = N\cdot \rightarrow CH_3\cdot + \cdot N = N\cdot \qquad [2B]$$

$$\cdot N = N\cdot \rightarrow N_2 \qquad [2C]$$

π bond energy of nitrogen, $-\Delta H$ of reaction [2C], to be 338 kJ mol^{-1}. In his opinion a reasonable upper limit was obtained. His arguments indicate that two bond rupture in gas phase diazene decomposition would lead to a transition state configuration of low energy, less than the weakest bond dissociation energy, represented by reaction [2A] or [2B]. Therefore the enthalpy change of reaction [2A] or [2B] would be greater than the observed activation energy and the value of the second π bond energy would be unreasonable high. Thus, Benson favoured one bond scission.

Special Techniques for Gas Phase Pyrolysis

In this section certain special techniques which have been used in the study of diazene pyrolysis in the gas phase are reviewed, briefly, and some references are given.

(1) Very Low Pressure Pyrolysis

Pyrolysis takes place in a flow reactor at very low pressure. Reactants and products are monitored in the early stages so that secondary reactions are kept to a minimum and unimolecular reactions can be studied directly. A disadvantage is that rate constants are obtained in the low pressure region and RRKM calculations have

to be performed to obtain high pressure rate constants. Even so, either the high pressure activation energy or pre-exponential factor has to be known or estimated independently. Application to diazenes is discussed in reference (2).

(2) **Laser Powered Homogeneous Pyrolysis**

The use of a pulsed IR laser to provide the thermal energy to an absorbing non-reactive gas, which transfers its energy to the reactive substrate in a flow through reaction vessel, has the advantage that there is no surface component to the substrate reaction. The one reported reaction, azoisopropane, gave the Arrhenius equation of $\log [k/s^{-1}] = 13.9 - 172\ kJ/2.3\ RT$ which the authors suggest, in contrast to some previous findings (16), is for a concerted pathway in the decomposition.

(3) **Coherent anti-Stokes Raman Spectroscopy, CARS**

This method involves pulsed photolysis, which, in the example cited, is azomethane at 355 nm. After a variable delay, a separate analysing laser system probes the CARS susceptibility of the excited sample volume. Exciting and probing beams provide a time profile of *ca.* 7 ns and a spectral resolution of 1 cm^{-1}. The results with azomethane indicate that nitrogen has an appearance time of less than 2 ns. This implies that the reaction mechanism involves no diazenyl intermediate† having a lifetime longer than 2 ns (17).

Reactions in the Liquid Phase

In the liquid phase, thermolysis of diazenes has been studied by a variety of methods. Some of the more recent studies and the main conclusions drawn are listed below. One bond scission is favoured in the liquid phase.

(1) Newman and others (19-23) have employed high pressure, to several thousand atmospheres, and solvent viscosity techniques. The volume of activation,

---

† *i.e.* $CH_3 - N = N\cdot$

$\Delta V^{\neq} = -RT(\Delta \ln k/\Delta P)_T$ for nitrogen formation was measured. These studies have shown that certain diazenes, termed "one bond scission" initiators[††], have large positive activation volumes (such as 18 to 21 $cm^3\ mol^{-1}$ in various solvents for 1-(4-nitrophenyl)-2-triphenylmethyldiazene). Others, termed "two-bond scission" initiators have small activation volumes (+5 $cm^3\ mol^{-1}$ for azocumene). Also, attempts have been made to relate the two types to the viscosity of the solvent. Rate constants of "one-bond scission" initiators should decrease as solvent viscosity increases and rate constants of "two-bond scission" initiators should be independent of solvent viscosity.

(2) A stereochemical approach has been taken by some workers. Thermolysis of some optically active diazenes has produced results which are interpreted in favour of one-bond cleavage (26). Photolysis of certain optically active *trans* diazenes seems to give *cis* diazenes which react by one-bond cleavage (25).

(3) The study of secondary deuterium kinetic isotope effects by Seltzer and Dunne (24), using the successive deuteration of the α carbon, indicated one bond scission for unsymmetrically substituted diazenes.

(4) Both ^1H and ^{15}N CIDNP spectra have been interpreted in favour of one-bond fission (18).[‡]

Potential Energy Surface

A potential energy surface has been calculated for azoethane (27) using the MNDO approximation to molecular orbital theory. A stepwise cleavage of azoethane was favoured, energetically, over the concerted mode of decomposition. Also, the

---

†† Initiators in the sense of initiating other radical reactions.

‡ Also, when cis-1-cumyl-2-phenyldiazene decomposed in the presence of triphenylmethyl radical a small yield of 1-phenyl-2-triphenylmethyldiazene was obtained, indicating that the phenyl diazenyl radical had been formed.

calculated activation energy for the stepwise cleavage is in reasonable agreement with the experimental measurements.

Objectives

The first objective of this study was to establish the main features of the pyrolysis of pure 1-methyl-2-phenyldiazene. The second was to isolate the elementary fission reaction and then to compare the results with the pyrolysis of azomethane and azobenzene, which had just recently been investigated. This comparison would help to clarify the role of one and two bond scission of mixed diazenes. Only the first objective has been achieved.

II Experimental

1. Preparation of 1-Methyl-2-Phenyldiazene and Purification of Propene

a. Synthesis

The method, essentially, was that described by Ioffe and Stopskii (29). One mole of freshly distilled phenylhydrazine†, 100 mls of diethyl ether, and 0.5 gm of hydroquinone were added to a 500 ml round-bottomed flask fitted with a dropping funnel, thermometer, and a reflux condenser. To this clear mixture was slowly added with stirring 109.6 gm of formalin* solution. The temperature during addition was maintained below 5 °C by means of an ice bath. Upon the addition of formalin the yellow solution became turbid; however, after one-third of the formalin solution had been added it became homogeneous.

Upon the further addition of 10 mls of formalin the yellow solution again became heterogeneous. Stirring was continued for one-half hour after completion of the addition and the reaction flask was removed from the ice bath after the addition was completed. The aqueous layer was separated and then washed three times with 50 mls of diethyl ether. The combined etheral phases were dried over anhydrous potassium carbonate and the ether was removed on a flash evaporator while bubbling nitrogen gas through the solution.

About 125 mls of the slightly turbid oily residue was added to a 500 ml 3-necked round-bottomed flask. An equal volume of a four percent solution of potassium hydroxide in ethylene glycol was added and the resulting purple solution was distilled under vacuum at 5 mm.

The distillation was carried out over three days, and three batches of the same

† Distilled at 110 °C and 2 mm.

* 35.6% formaldehyde; 10-15% methanol; water.

fraction were collected. Between collections the reaction flask was vented. The yield of yellow distillate decreased with each distillation giving a total yield of 25%.

b. Purification of Batch A

The procedure, as described above, was repeated and the two lots were combined. The combined lots, designated Batch A, were used for all runs in the packed reaction vessel.

The combined lots were stored over activated molecular sieve* and then eluted through an anhydrous magnesium sulfate column† with dry pentane. Part of the solvent was removed by distillation on a rotary evaporator. The 1-methyl-2-phenyldiazene was then passed through a silica gel†† column§ using dry pentane. Again, part of the solvent was removed by means of a flash evaporator. The remainder of solvent, about one-third, was removed under 2-3 mm Hg at 0°C for five minutes.

Further purification was carried out on a spinning band column. The bleed was enclosed in a bag of dry nitrogen gas and 1-methyl-2-phenyldiazene was distilled at 45°C under 8 mm pressure. The first 2 mls of distillate were discarded, the column heater was kept at ambient temperature, and the column was spun as slowly as possible. The distillation was stopped by venting with dry nitrogen gas and the distillate was stored under dry nitrogen gas at 4°C in the dark.

A gas chromatogram▽ of this distillate indicated that the only impurity was aniline, in one percent concentration. Therefore the 1-methyl-2-phenyldiazene was

---

* 4Å, dried at 120°C for 48 hours.

† 5 cm x 1 cm I.D.

†† Dried at 120°C for 48 hours.

§ 4 cm x 1 cm I.D.

▽ Column - 6' x ¼". 3% OV-17; T = 130°C.

redistilled on the spinning band column. As before, the first and last 2 mls of distillate were discarded. The pressure was set at 9 mm and the distillate was collected at 47 ° C. For this distillation the apparatus was wrapped in towels to prevent possible photolysis.

The liquid collected from the second distillation was subdivided into break-seal vials.

A gas chromatogram of the liquid showed that the sample contained 99.57% 1-methyl-2-phenyldiazene, with aniline as the only impurity.

c. Purification of Batch B

For all subsequent runs the 1-methyl-2-phenyldiazene used was prepared as described below and designated Batch B. Two crops of 1-methyl-2-phenyldiazene were synthesized for this batch, designated Lots 1 and 2, and were purified in the same manner.

After distillation from the reaction flask, the 1-methyl-2-phenyldiazene in methylene chloride was extracted three times with 50 mls of one molar hydrochloric acid and then dried over anhydrous potassium carbonate. Part of the solvent was removed on a rotary evaporator and the remainder by vacuum distillation under 2-3 mm Hg at 0 ° C for five minutes.

As with batch A, the 1-methyl-2-phenyldiazene was then distilled on the spinning band column. The bleed was encased in a bag of dry helium and the apparatus was shrouded in a black cape during distillation. As before, the first 2 mls of distillate were discarded and the fraction boiling at 45 ° C at 9 mm pressure was collected.

A gas chromatogram* of lot 1 showed the presence of 1.7% of an unknown impurity and 1.0% of aniline. A gas chromatogram of lot 2 indicated only 1.2% of

* Column - 6' x ¼" 3% OV-17; T = 130 ° C.

the unknown impurity. Subsequent distillation on the spinning band column removed all of the aniline but 1.0% of the unknown impurity* remained in both lots. The product was subdivided and stored in 5 ml ampoules under dry helium. Further purification was carried out by preparative gas chromatography.

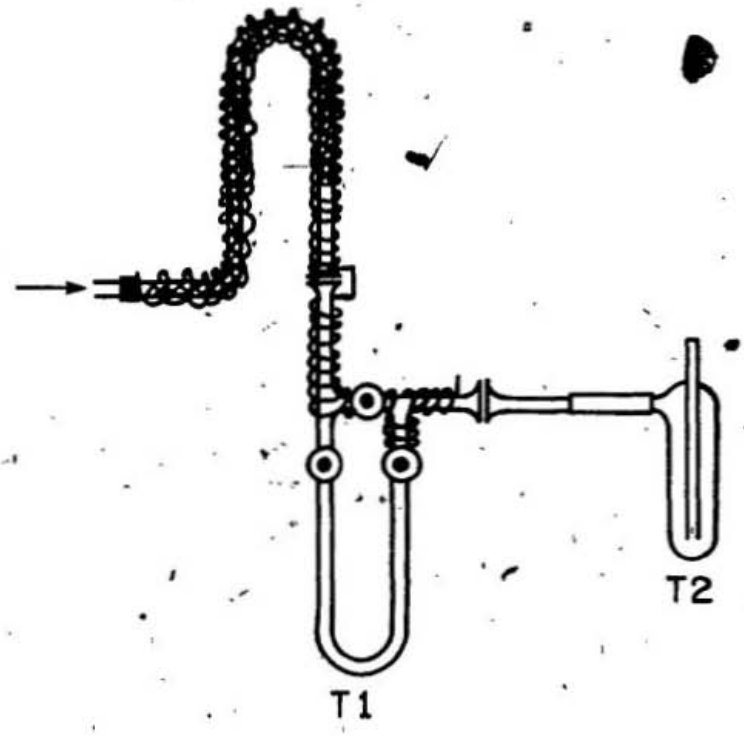
At first, 30 μl portions of the ninety-nine percent 1-methyl-2-phenyldiazene were injected into the gas chromatograph†. The column effluent was swept into an apparatus, like that illustrated in figure 1, to separate the 1-methyl-2-phenyldiazene from the other impurities. Appropriate parts of the apparatus were maintained at 90°C to prevent condensation of the effluent. The 1-methyl-2-phenyldiazene was collected in the U-trap as it eluted from the gas chromatograph; the rest of the gas chromatograph effluent was by-passed. To make the preparative gas chromatograph more efficient an 8' x ½" 3% OV-17 column was made so that a 50 μl sample could be injected. Ten injections and collections were made, then the trap containing helium was isolated and connected to the additive section of the vacuum line via the O-ring connection. After evacuation, the 1-methyl-2-phenyldiazene was transferred to the U-trap which was maintained at -45°C with an acetone bath cooled by dry ice. During transfer, the reaction vessel was maintained at less than 200°C, because the 1-methyl-2-phenyldiazene passed through it, and the manifold valve on the back side of the U-trap was open to the pumps to remove any volatile impurities. After distillation the manifold valve was closed, the reactant storage trap was cooled with liquid nitrogen, and the U-trap was warmed in order to transfer the 1-methyl-2-phenyldiazene to its storage section. After the transfer the distillation was repeated at a maximum 1-methyl-2-phenyldiazene pressure of 1 mm.

7 μl of distillate was transferred to the benzene O-ring section for injection onto the gas chromatograph. If the gas chromatogram of the sample indicated that the

---

* See Appendix B for discussion.

† 8' x ¼" 3% OV-17 column; T = 85°C.



→ Effluent from gas chromatograph

Nichrome heating coil and Kaowool insulation

Teflon valve with rubber O-rings or all teflon valve

Copper

Glass

O-ring joint

T1 Trap for Diazene

T2 Trap for discarded materials

Figure 1. Collection apparatus for column effluent.

total concentration of the unknown impurity and aniline was greater than 0.01 percent the preparative gas chromatograph procedure was repeated. If the concentration of the 1-methyl-2-phenyldiazene was greater than 99.99% it was transferred back to the storage section ready for use.

A high resolution mass spectrum of a sample prepared in this way is shown and discussed in Appendix A, Table 11.

d. Purification of Propene

Propene (Matheson Research Grade, Min. Purity 99.7%) was introduced into the U-trap of the vacuum line. It was then distilled from a hexane/liquid nitrogen trap (-94°C) to an isopentane/liquid nitrogen trap (-160°C) on the additive storage section. After distillation the U-trap was warmed to ambient temperature and opened to vacuum. The traps were then reversed to collect the propene back into the U-trap. The "backend" of the U-trap was pumped during this distillation to remove any carbon dioxide that may have been present. After distillation the storage section was warmed to ambient temperature and evacuated. Again the slurries were reversed to distil the propene back into the storage section.

2. Vacuum Line

The vacuum line, illustrated in figure 2, was assembled in the following manner.

a. Pumping System

A Welch Duo-Seal model 1400 rotary pump was used with a Balzers oil diffusion pump. A vacuum of less than 2×10^{-6} Torr, as measured by means of a McLeod gauge, was always obtained before a run was started.

b. Toepler Pumps

Two toepler pumps, illustrated in figure 3, were employed in the line. The first collected the non-condensable fraction into a calibrated gas burette with the aid of an automated solenoid valve located at the inlet to the mercury reservoir line. This was accomplished by having three electrical contacts protruding into the toepler pump. One, located above the top float valve, switched the solenoid valve from a venting mode to an evacuating mode. The second lead was located at the top of the reservoir and switched the valve back to the venting mode. The third lead, located at the bottom of the reservoir, was common to the other two.

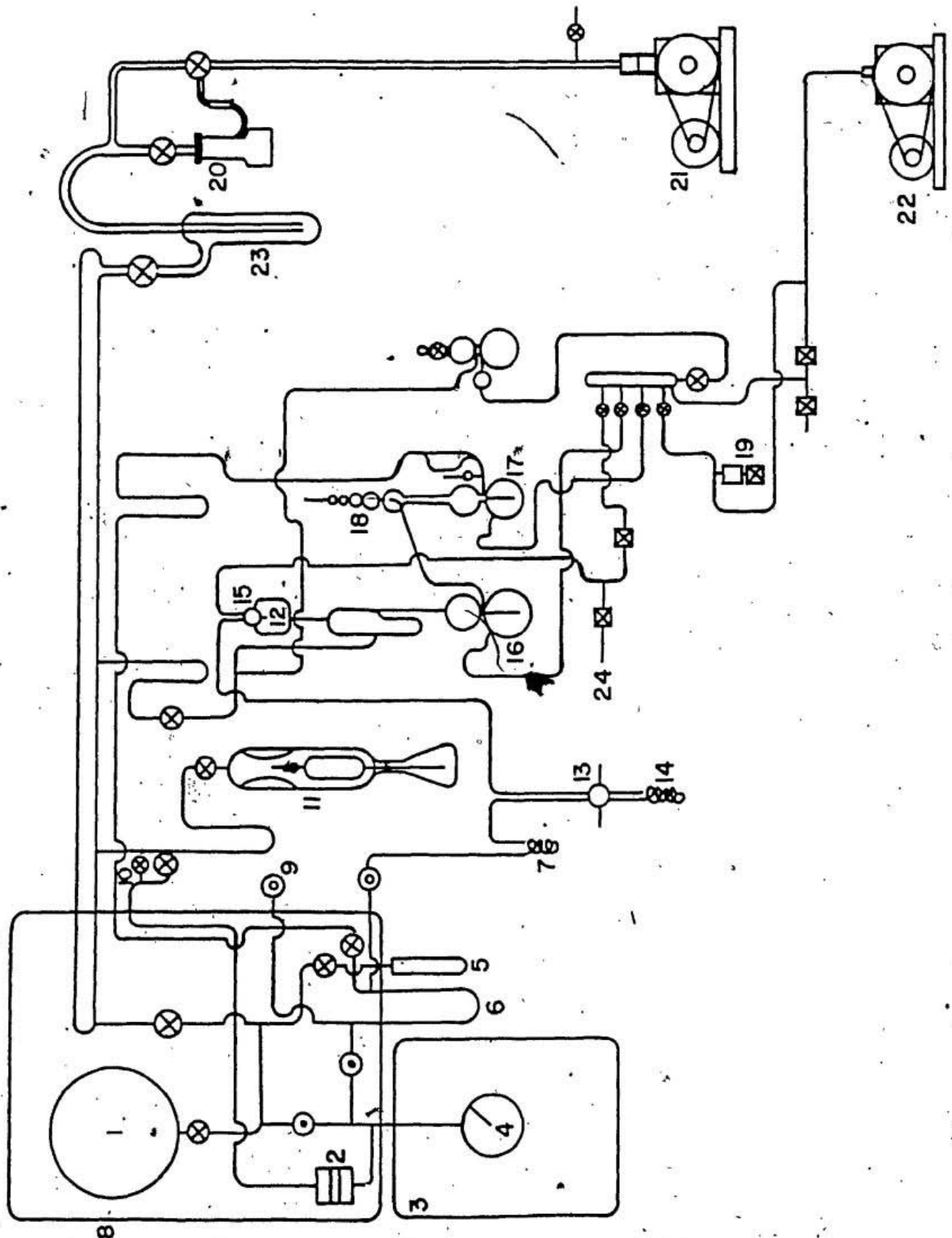
After the gas was collected and measured the float valve leading to the manifold from the second toepler pump was closed and the gas was transferred to the second pump. After all of the gas was transferred, using twenty strokes of the second toepler pump, the mercury level was raised to the Y of the gas transfer loop.

As illustrated in figure 4, when the gas transfer loop valve was switched, the collected gas was swept onto the molecular sieve column and the float valve below the loop closed. To open this float valve, which was under pressure, after the sample had been chromatographed, it was necessary to set the gas chromatograph valves, as illustrated in figure 4. The helium flow was then stopped and the loop was partially evacuated, allowing opening of the valve.

1 5 L mixing vessel
2 Mks capacitance manometer
3 Reaction vessel oven
4 Reaction vessel
5 Diazene storage trap
6 U-trap
7 O-ring joint
8 Air bath
9 Line to additive storage section
9' Additive storage section outside of air bath
10 Vent
11 McLeod gauge
12 Loop for CH_4 and N_2
13 6-Port valve on chromatograph
14 MS column on sample loop of chromatograph
15 6-Port valve
16 Toepler pump
17 Toepler pump
18 Gas burette
19 Automatic toepler pump valve
20 Oil diffusion pump
21 Rotary pump
22 Rotary pump
23 Main trap
24 Helium supply

⊙ Varian valve, viton seal
◉ Varian valve, polyimide seal
⊗ Stopcock
⊠ Metal valve

Figure 2. Schematic of initial vacuum line.


1
2
3
4
5
6
7
8
9
11
12
13
14
15
16
17
18
19
20
21
22
23
24

1 6 Port valve. Ports 3, 4 to sample collection loop. Ports 1, 6 joined. Port 2 helium supply and low vacuum. Port 5 exit to gas chromatograph. Refer to Figure 4.

2 Sample collection loop for CH_4 and N_2.

3 Float valve.

3' Double float valve.

4 Toepler pump, manual.

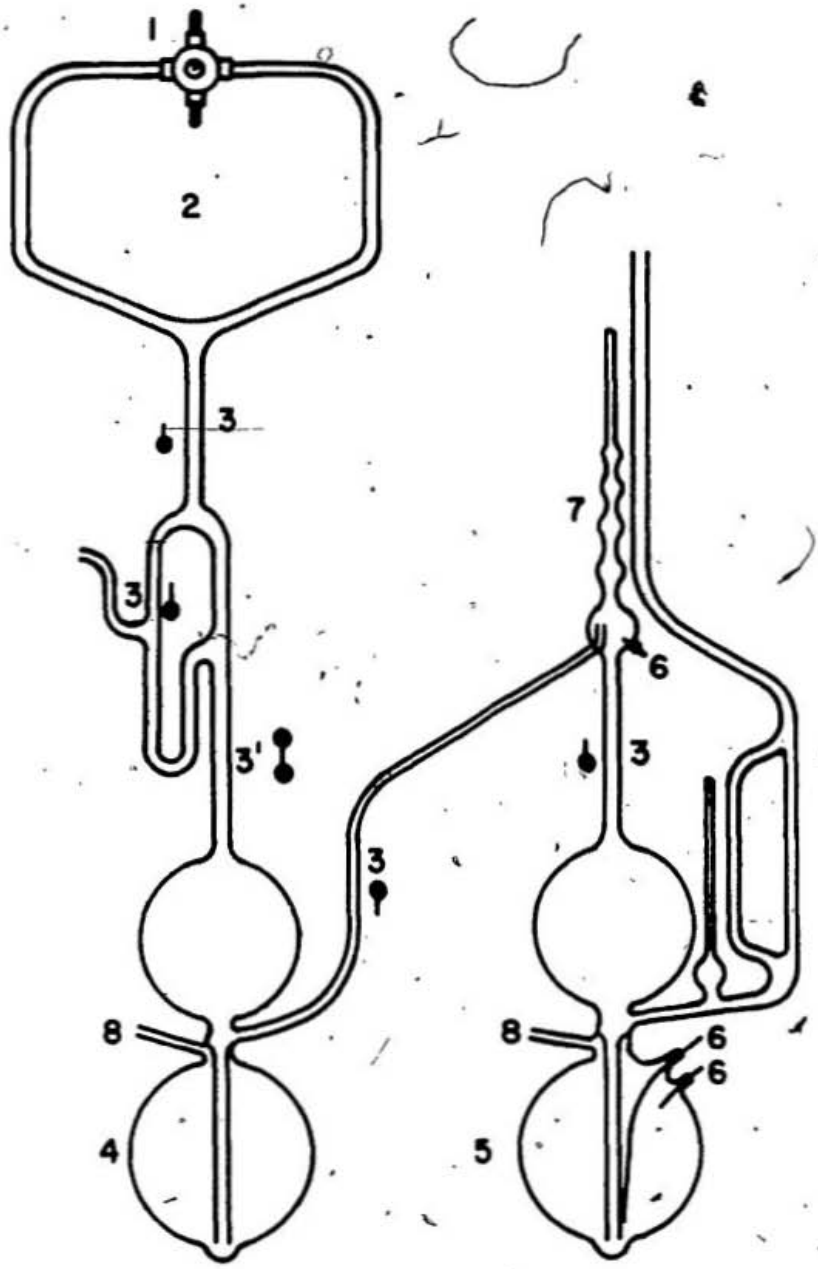
5 Toepler pump, automatic.

6 Electrical contacts.

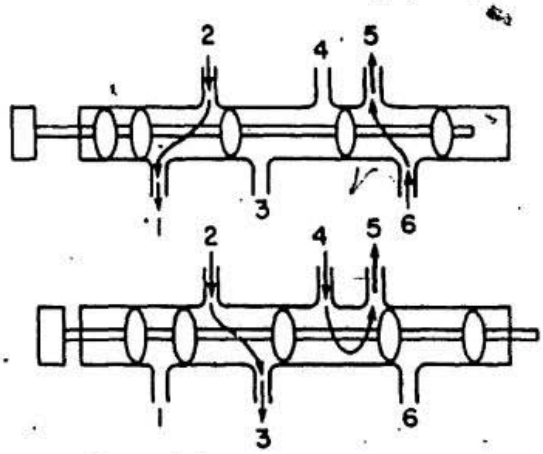
7 Gas burette.

8 Connections are shown in Figure 8.

Figure 3. Schematic of Toepler pumps.


1
2
3
3
3'
3
7
6
3
8
4
8
6
6
5

SIX-PORT VALVE ON LINE IN CH_4, N_2 COLLECTION LOOP



Position during collection of sample

Position during transfer to chromatograph

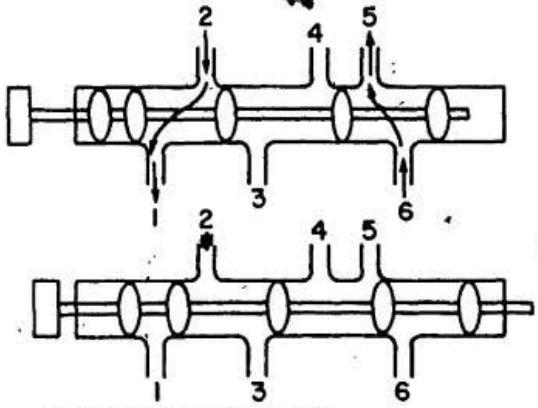
3,4 To sample loop

1,6 Connected to each other

5 To chromatograph

2 Helium supply.

SIX-PORT VALVE ON CHROMATOGRAPH



Position during transfer of sample to chromatograph

Position during evacuation of sample loop
• Partial vacuum

2 From six-port valve on line

1,6 To molecular sieve column

5 To injector B on chromatograph

3 Plugged

During early experiments an auxiliary helium supply was connected at 4.

Figure 4. Schematic of switching valves on vacuum line and gas chromatograph.

c. Pressure Gauge

Measurement of the initial pressure of the 1-methyl-2-phenyldiazene was made using an MKS Baratron 170M-26BM 100 mm head connected to an MKS Baratron 315BH-100 readout module, a 170M-6C Electronic Unit and a 170M-35 Temperature Compensator.

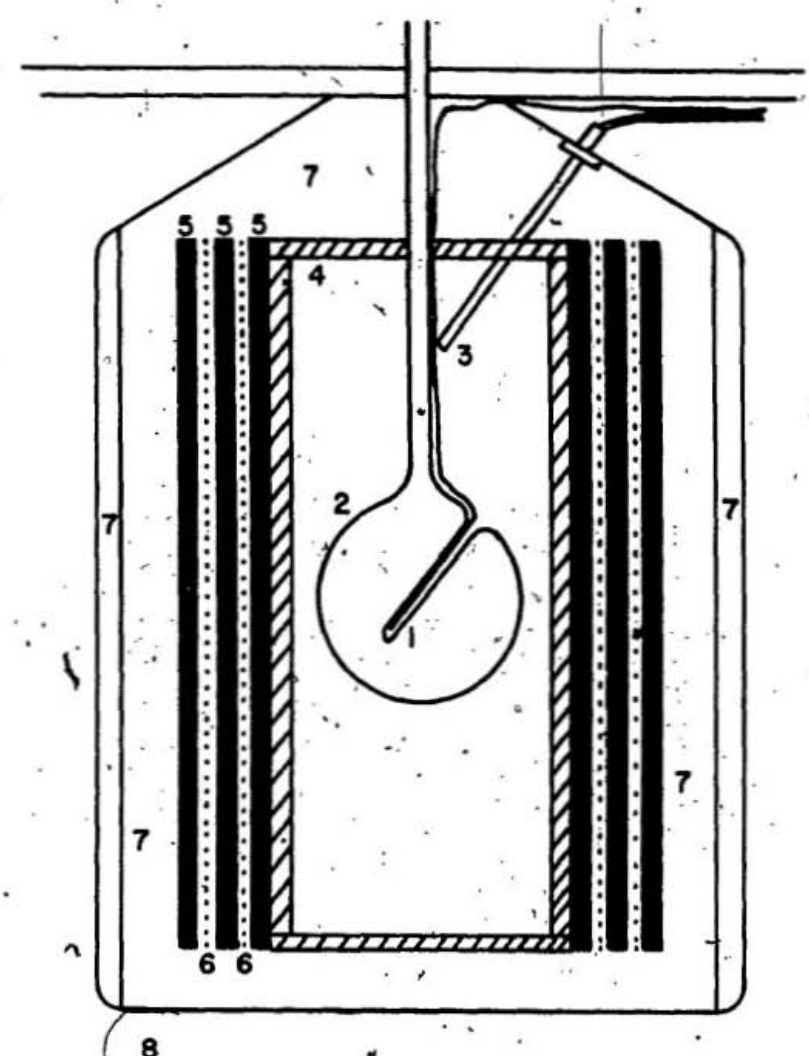
d. Reaction Vessels

a) The first part of this study employed a pyrex vessel packed with 5 cm pyrex glass tubes which were fire polished on both ends. The vessel had a volume of 980.0 ml and a surface to volume ratio of 1.17 cm^{-1}.

b) The next set of experiments were carried out in an unpacked pyrex vessel. This reaction vessel had a volume of 1007.4 ml and a surface to volume ratio of 0.547 cm^{-1}.

e. Reaction Vessel Oven

The central part of the oven, shown in figure 5, consisted of an aluminum cylinder, with diameter 0.2 m and length 0.5 m, fitted with an aluminum bottom and lid. The cylinder was made of 0.8 cm stock and the lid and bottom of 2 cm stock. Three heaters of Kanthal wire were wound around the cylinder at the lower and upper ends, and in the middle. These, controlled by Variacs, were turned on continuously. A third, outside of these, was controlled by a Thermodyne-Precision relay connected to a platinum resistance probe. Heaters were insulated from the cylinder and one another by asbestos. Kaowool, a metal can, a second layer of Kaowool, and finally a layer of aluminum foil surrounded the cylinder and heaters. Kaowool was also packed in the space between the top of the lid and the bottom of the air bath, a distance of 10 cm.



1 - Thermocouple

2 Reaction vessel

3 Thermostat probe

4 Aluminum cylinder, bottom and lid

5 Asbestos

6 Heaters

7 Kaowool

8 Metal can

Figure 5. Schematic of reaction vessel oven.

A slot in the lid allowed the thermocouples and platinum resistance probe to extend into the cylinder, and also accommodated the neck of the reaction vessel.

Two chromel-alumel thermocouples were placed in the reaction vessel well after the leads were insulated with glass wool. They were calibrated at the melting points of tin (231.9 °C) and of lead (327.4 °C), using reference samples which were obtained from the National Bureau of Standards of the United States. The results of calibration are given in the following table.

	Reference	TC#1†	TC#2†
Tin	231.9 °C	235.2±0.1 °C	234.0±0.1 °C
Lead	327.4 °C	332.0±0.1 °C	332.5±0.1 °C

† Temperature calculated from data supplied by R.P. Benedict. Fundamentals of temperature, pressure, and flow measurements. 2nd ed. Wiley. New York. 1977.

Temperatures were obtained by linear interpolation. TC#1 was connected to a Digitec Thermocouple Thermometer and TC#2 was read directly in millivolts and referenced to an ice-water slush bath.

f. Gas Chromatograph

The reaction products were analysed chromatographically as gas and as condensable (in liquid nitrogen) fractions. The gas chromatograph used was a Varian Aerograph Model 1700 with a thermal conductivity detector. Injector temperature was set at 100 °C, and detector temperature at 200 °C.

The gas fraction was analysed on a one meter 5Å molecular sieve column at 50 °C using a flow rate of the carrier gas, helium, of 30 milliliters per minute. The

column was activated at 200 °C for sixteen hours with carrier gas flowing through it.

The condensed fraction was analysed on an eight foot by one quarter inch stainless-steel column packed with three percent OV-17 on Gas Chrom W, again using a flow rate of the carrier gas, helium, of thirty milliliters per minute. The column was baked out once a week at 200 °C for sixteen hours with carrier gas flowing through it. Temperature programming was used for the condensable fraction: 100 °C for seven minutes, then 15 °C per minute to 200 °C for twenty minutes.

The gas chromatograph was calibrated for nitrogen, methane, benzene, toluene and subsequently for aniline and N-methylaniline.

g. Air Bath

The air bath was a thermostated asbestos box. The temperature was maintained at 105 °C to prevent the 1-methyl-2-phenyldiazene and products from condensing in the line.

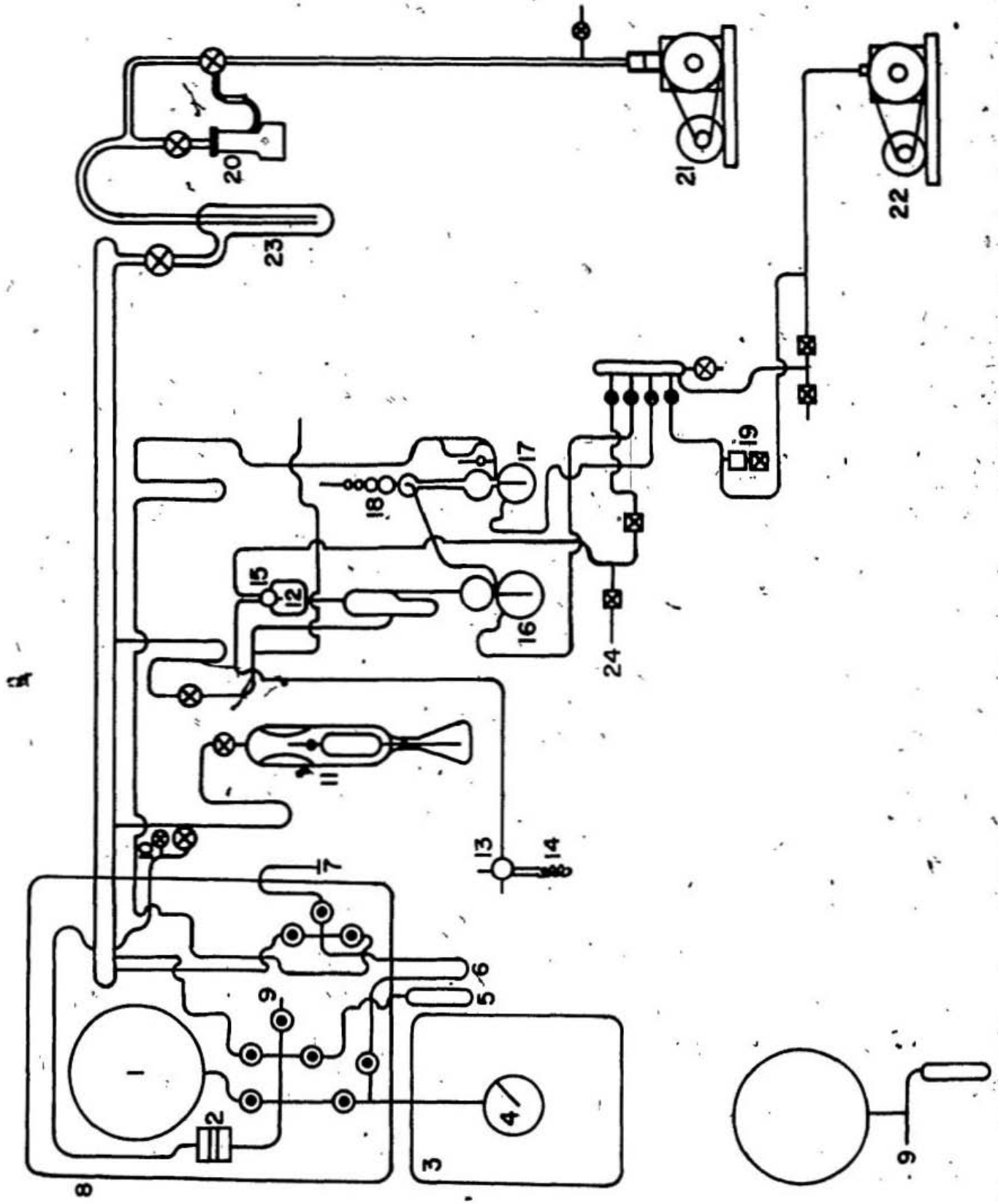
The design of the vacuum line inside the air bath, illustrated in figure 2, was used for the packed reaction vessel runs. Varian high vacuum valves with polyimide main seals and gaskets were used at the inlet and exit of the reaction vessel to prevent reactant and reaction products from dissolving in stopcock grease and to withstand the high temperatures of the air bath. Varian high vacuum valves with viton main seals were used on the helium sweep lines to prevent dissolution of reaction products in stopcock grease. Stopcocks, with silicone grease as lubricant were used elsewhere in the line inside the air bath.

The vacuum line inside the air bath was redesigned, as illustrated in figure 6, for subsequent experiments in which the unpacked vessel was used. These modifications, listed below, were made to alleviate some problems which were experienced with the previous design.

1 5 L mixing vessel
2 Mks capacitance manometer
3 Reaction vessel oven
4 Reaction vessel
5 Diazene storage trap
6 U-trap
7 Coiltrap
8 Air bath
9 Line to helium supply
10 Vent
11 McLeod gauge
12 Loop for CH_4 and N_2
13 6-Port valve on chromatograph
14 MS column on sample loop of chromatograph
15 6-Port valve
16 Töepler pump
17 Toepler pump
18 Gas burette
19 Automatic toepler pump valve
20 Oil diffusion pump
21 Rotary pump
22 Rotary pump
23 Main trap

⦿ Varian valve, polyimide seal
⊗ Stopcock
⊠ Metal valve

Figure 6. Schematic of redesigned vacuum line.


20
21
22
23
19
18
17
15
12
16
24
11
13
14
7
6
5
9
1
2
4
3
8
9

1. Varian polyimide valves were used in all parts of the vacuum line in which the 1-methyl-2-phenyldiazene was in contact. This prevented dissolution of the diazene in stopcock grease.

2. The helium sweep lines were removed because it was found that the condensed fraction was incompletely swept to the collection trap. Because of this, all results of chromatographic analyses of the condensed fraction for the packed reaction vessel had to be discarded. Also, there was apparently some leakage of helium through the valves which affected the analysis of nitrogen and methane.

   When the sweep lines were discarded, ports 3 and 4 on the gas valve of the gas chromatograph, figure 4, were plugged. Injector B of the gas chromatograph was then plumbed directly to the first helium supply.

3. A storage section was added to the line for additives.

3. Procedure

The procedure for the two reaction vessels was different because the vacuum line was modified after the packed vessel was removed. Also, when propene was used as an additive, the procedure was again different. Therefore the procedure for each reaction vessel, and with propene as an additive, will be outlined.

a. Packed Reaction Vessel

During a run, the following sequence of operations were performed. First, the appropriate parts of the vacuum line, illustrated in figure 2, were pumped down to less than 2×10^{-6} Torr. The 1-methyl-2-phenyldiazene was then degassed* twice, using liquid nitrogen. It was next warmed to 60 °C by means of hot water, and then introduced into the reaction vessel through the manifold. The pressure was monitored during the course of the reaction using the pressure gauge attached to the reaction vessel.

In order to stop the reaction the contents of the reaction vessel were vented to a U-trap which was immersed in liquid nitrogen. The fraction of products which passed through the U-trap was collected by means of an automatic toepler pump, until no gas remained in the transfer line as measured with an in-line McLeod gauge. The quantity of gas was measured in a calibrated gas burette, and then, with the aid of the second toepler pump and gas sampling valve, injected into the gas chromatograph.

The condensed fraction was warmed and swept, by means of helium flowing at 30 ml per minute for thirty minutes, to a collection trap which was immersed in liquid nitrogen. It was then rapidly warmed to 50 °C and swept into the gas

* Degassing is the procedure which involves warming a material to ambient temperature while the section of vacuum line containing the material is closed to vacuum. Then the material is condensed in liquid nitrogen and the section of vacuum line is again evacuated.

chromatograph.

b. Unpacked Reaction Vessel

The procedure for the experiments in which the unpacked reaction vessel was used differed from the one just described in the following ways. First, the procedure of sweeping the condensed fraction was abandoned and it was simply distilled from the U-trap to the benzene O-ring trap. The trap was then removed and 7 μl of the condensed fraction were injected into the gas chromatograph. Also, the pressure was not monitored during runs with the unpacked vessel because the pressure gauge was not directly connected to the reaction vessel.

c. Unpacked Reaction Vessel and Propene

The next series of experiments, for which mixtures of propene and 1-methyl-2-phenyldiazene were prepared, were also carried out in the unpacked vessel.

Before use, the propene, as well as the 1-methyl-2-phenyldiazene, were degassed twice in liquid nitrogen. A mixture was then prepared by introducing a measured pressure of diazene into the 5 liter storage vessel; propene was added quickly and the total pressure measured. The mixture was allowed to mix for about twelve hours. A series of runs was then carried out using the stored mixture. Only the fraction which passed through the liquid nitrogen trap was analysed in this set of experiments.

After completion of the main part of this study a number of runs were carried out for which the mixing time was as short as possible, about 30 minutes.

III Results

1. Definition of Rate Constant

To determine the initial rate of the reaction the conversion of reactant, as measured by production of N_2, was kept to three per cent or less.

To determine the amounts of N_2 and CH_4, the non-condensable fraction, the number of moles of total gas was first measured in a gas burette. The gas was then transferred to a gas chromatograph where N_2 and CH_4 were separated on a 5A molecular sieve column. The gas chromatographic response for each gas was measured. Therefore the ratio of N_2 to CH_4 could be calculated. This ratio times the total number of moles of gas gave the amounts of N_2 and CH_4 in moles.

The rate of production of a product was defined as

$$\text{rate} = \frac{(\text{product})}{V \times t}$$

where (product) was the number of moles of a product found at the end of reaction time t, in seconds, in a reaction vessel of volume V, in liters.

The apparent first order rate constant was defined as

$$k = \frac{\text{rate}}{[\text{MPDA}]_i}$$

where rate was the rate of N_2 production expressed in mol l^{-1} s^{-1} and $[MPDA]_i$ was the initial concentration of 1-methyl-2-phenyldiazene in moles per litre. The order for the rate of formation of a product was defined as the slope of the plot of ln[rate] versus $\ln[MPDA]_i$.

2. Unpacked Vessel

a. Products

Two fractions of products were collected, that which passed through a liquid nitrogen trap and that which condensed.

The non-condensable fraction† was analysed for nitrogen and methane by the procedure described above.

The condensed fraction* was distilled from the warmed U-trap to an O-ring trap immersed in liquid nitrogen, also as described above. There was no apparent residue in the U-trap after distillation. The O-ring trap was then warmed, the seal broken and 7 μl of the liquid was injected onto the gas chromatograph.

Semi-quantitative analysis of the products of the condensed fraction was attempted by injection of a constant volume of the condensed fraction onto the gas chromatograph. By assuming that the condensed fraction was 100 percent 1-methyl-2-phenyldiazene, the total volume of the fraction could be calculated from the number of moles of reactant introduced and its density (See Appendix C which contains a summary of all analytical results.).

Identification of the products in the condensed fraction was accomplished by retention time of known compounds and by gas chromatography-mass spectrometry (see Appendix B).

Table 1 lists the products and the mole percent for a sample run. Analysis of the condensed fraction was, in some cases, not sufficiently reliable to be used for kinetic study. In fact no kinetic treatment of the condensed fraction is reported in this thesis.

b. Yield versus Time Plots

Yield *versus* time plots were made of nitrogen and methane at two temperatures, 559.0 K and 529.4 K. Both series of experiments had an initial 1-methyl-2-

---

† Attempts to detect ethane by mass spectrometry, at the beginning of this study, were not successful. However, in a run carried out after completion of the study, the mass spectrum was consistent with the presence of about one mole percent ethane in the non-condensable fraction.

* Of certain runs.

Table 1. Products and mole percent for a sample run at 559.0 K.

Products	Mole %
Nitrogen	50.5
Methane	19.4
Diazenes†	10.4
Aniline	7.0
N-Methylaniline	5.8
Toluene	0.2

† Only one peak appeared on the packed column, but 1-phenyl-2-ethyldiazene and 1-benzyl-2-methyldiazene are separated on the DB-1 capillary column (see Appendix B).

phenyldiazene concentration of approximaely 1.5 x 10^{-4} mol l^{-1}, and, as can be seen from figures 7 and 8 respectively, the yield of products increases linearly with time. Linear regression analysis* was performed on both sets of data, and Tables 2 and 3 show that methane curves have small negative intercepts while the nitrogen curves also have small intercepts, one positive and the other negative.

c. Order Plots

Order plots, as defined above, were made for nitrogen and methane at two different temperatures, 559.0 K and 529.4 K. The experiments at 559.0 K were carried out for one thousand seconds to 2.5 percent reaction while those at 529.4 K were carried out for two thousand seconds to 0.50 percent reaction. The order plots are shown in figures 9 and 10. Regression analysis was also performed on these sets of data, Tables 4 and 5, to give the apparent kinetic order for nitrogen and methane at 559.0 K and 529.4 K.

d. Addition of Propene

In order to study the effect upon the reaction of the addition of a radical scavenger (6) propene was added to the reactant at 559.0 K. Two sets of experiments were carried out with 1.17 percent and 11.0 percent 1-methyl-2-phenyldiazene in propene. All experiments were carried out for one thousand seconds, and the mixtures were equilibrated for about 12 hours.

As can be seen from Table 6, within experimental error, the average first order rate constant for the runs with propene is the same as those without propene.

Order plots for nitrogen and methane are shown in figure 11. Regression analysis of both sets of data produce the orders shown in Table 6.

* Regression analysis was carried out as described by Wentworth (30,31). The equations were written into a Basic program and run on a HP 85A computer.

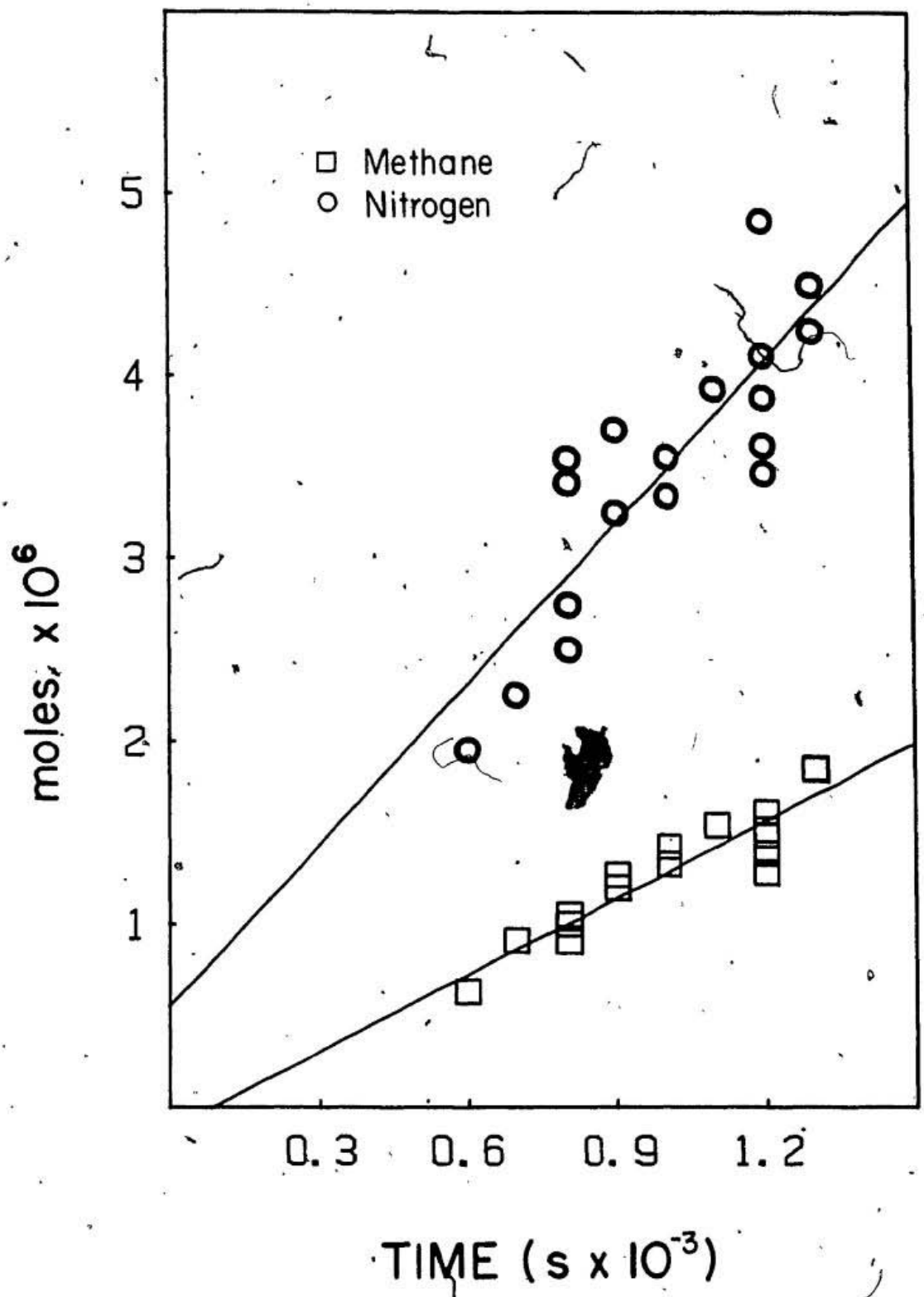


Figure 7. Yield versus time plots for nitrogen and methane at 559.0 K in unpacked reaction vessel.

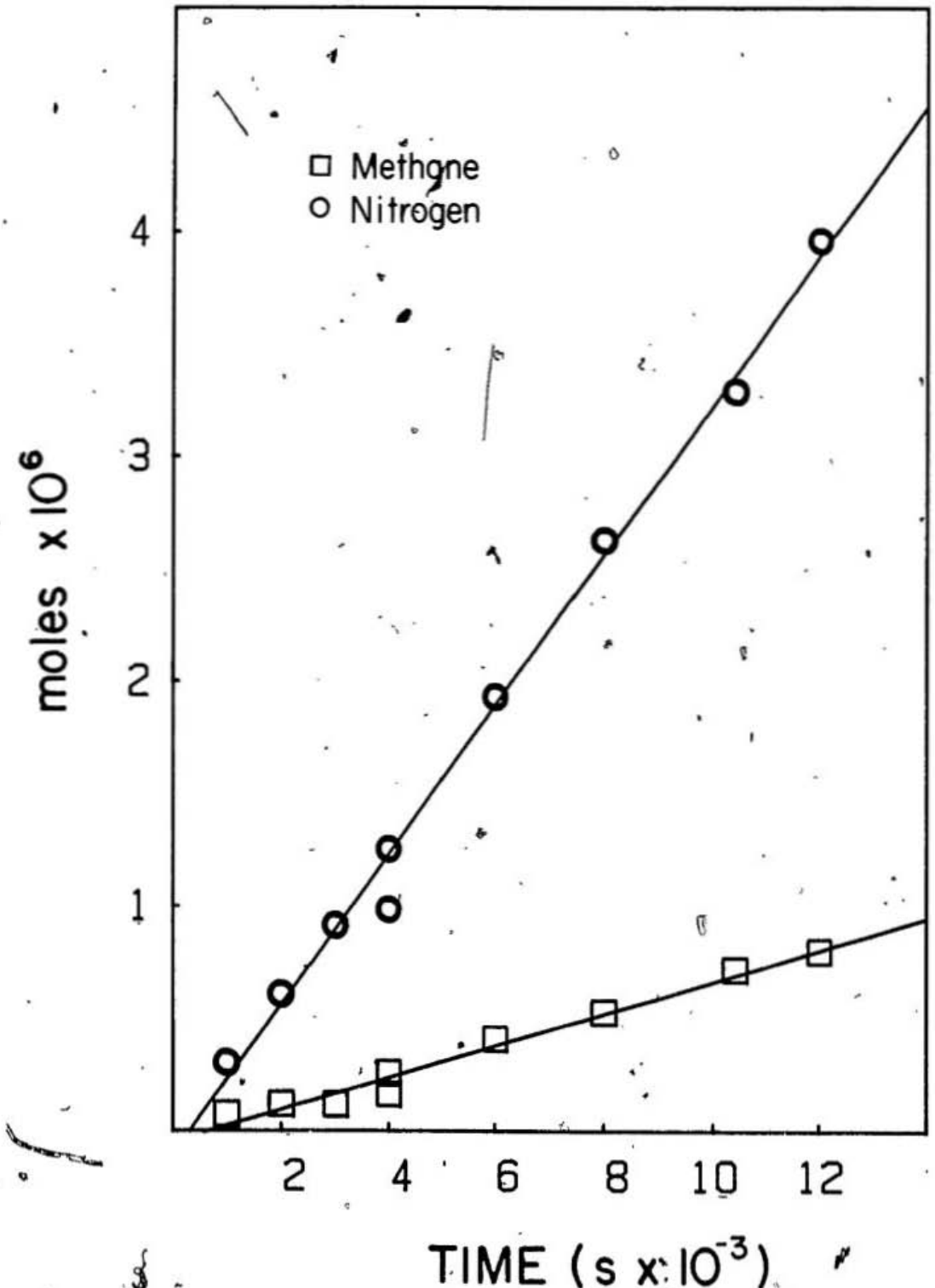


Figure 8. Yield versus time plots for nitrogen and methane at 529.4 K in unpacked reaction vessel.

Table 2. Yield *versus* time data and calculated slopes and intercepts for nitrogen and methane at 559.0 K in unpacked vessel.

Yield versus Time*		
Time x 10^{-2} s	N_2 moles x 10^6	CH_4 moles x 10^6
6.00	1.953	0.6325
7.00	2.253	0.9141
8.00	3.542	0.9071
8.00	3.410	1.002
8.00	2.500	1.002
8.00	2.744	1.052
9.00	3.701	1.268
9.00	3.246	1.198
10.00	3.338	1.422
10.00	3.550	1.326
11.00	3.927	1.539
12.00	3.463	1.384
12.00	3.615	1.279
12.00	3.878	1.485
12.00	4.109	1.515
12.00	4.850	1.609
13.00	4.246	1.842
13.00	4.498	1.848

* $[\text{1-Methyl-2-Phenyldiazene}]_i$ $(1.50 \pm 0.02) \times 10^{-4}$ mol l^{-1}, Temperature 550.0 K

Intercept (nitrogen) $(5.5 \pm 4.6) \times 10^{-7}$

Intercept (methane) $(-1.1 \pm 1.4) \times 10^{-7}$

† All errors are standard deviations.

Table 3: Yield *versus* time data and calculated slopes and intercepts for nitrogen and methane at 529.4 K in unpacked vessel.

Yield versus Time*

Time x 10^{-3} s	N_2 moles x 10^6	CH_4 moles x 10^7
1.000	0.3062	0.7830
2.000	0.6100	1.224
3.000	0.9146	1.196
4.000	0.9852	1.646
4.000	1.253	2.592
6.000	1.930	4.113
8.000	2.625	5.297
10.400	3.287	7.190
12.000	3.596	8.009

* $[1\text{-Methyl-2-Phenyldiazene}]_i$ $(1.56 \pm 0.01) \times 10^{-4}$ mol l^{-1}

Temperature 529.4 K

Intercept (nitrogen) $(-3.1 \pm 7.7) \times 10^{-8}$

Intercept (methane) $(-4.1 \pm 2.7) \times 10^{-8}$

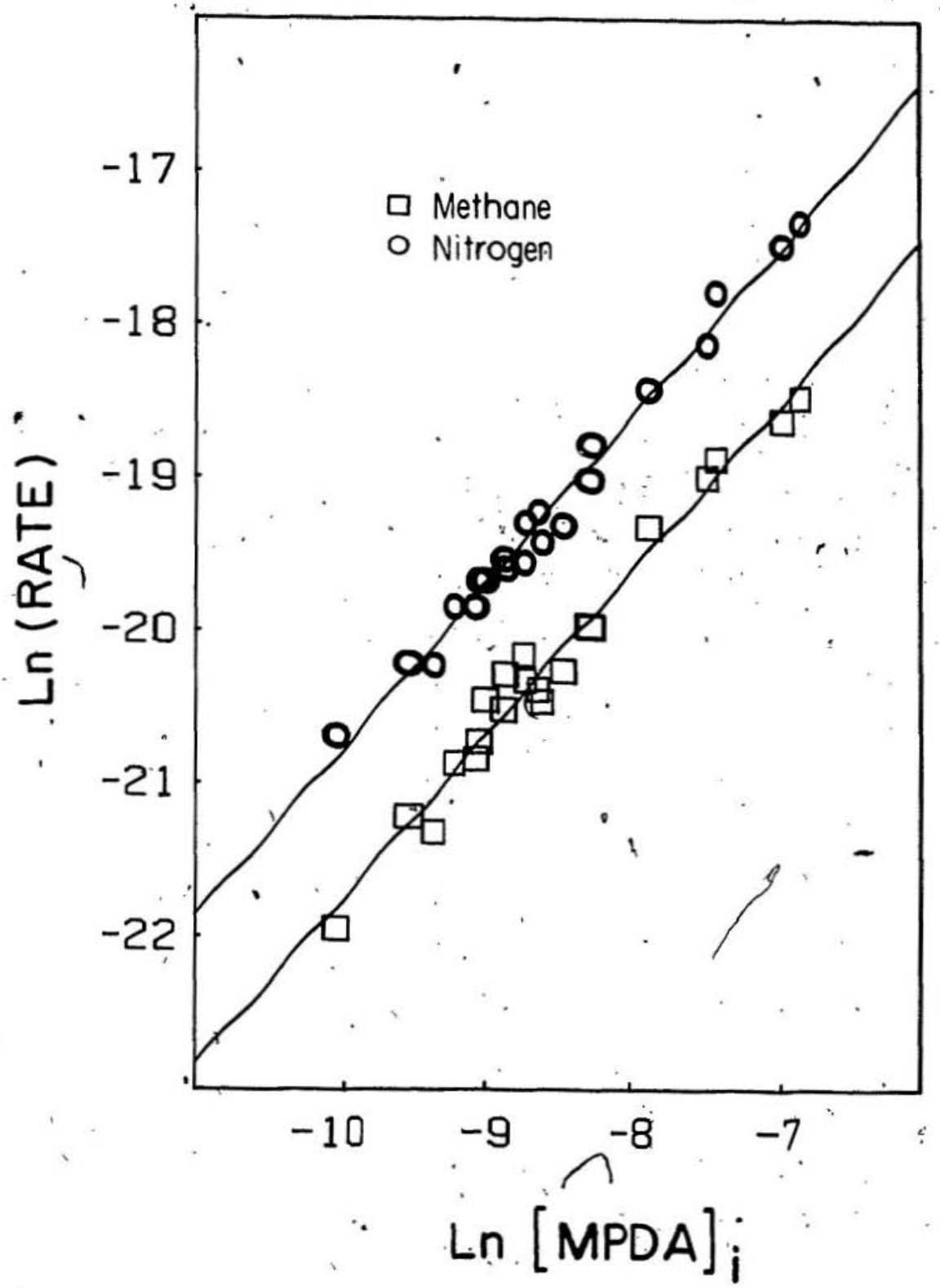


Figure 9. Order plot for nitrogen and methane at 559.0 K in unpacked reaction vessel.

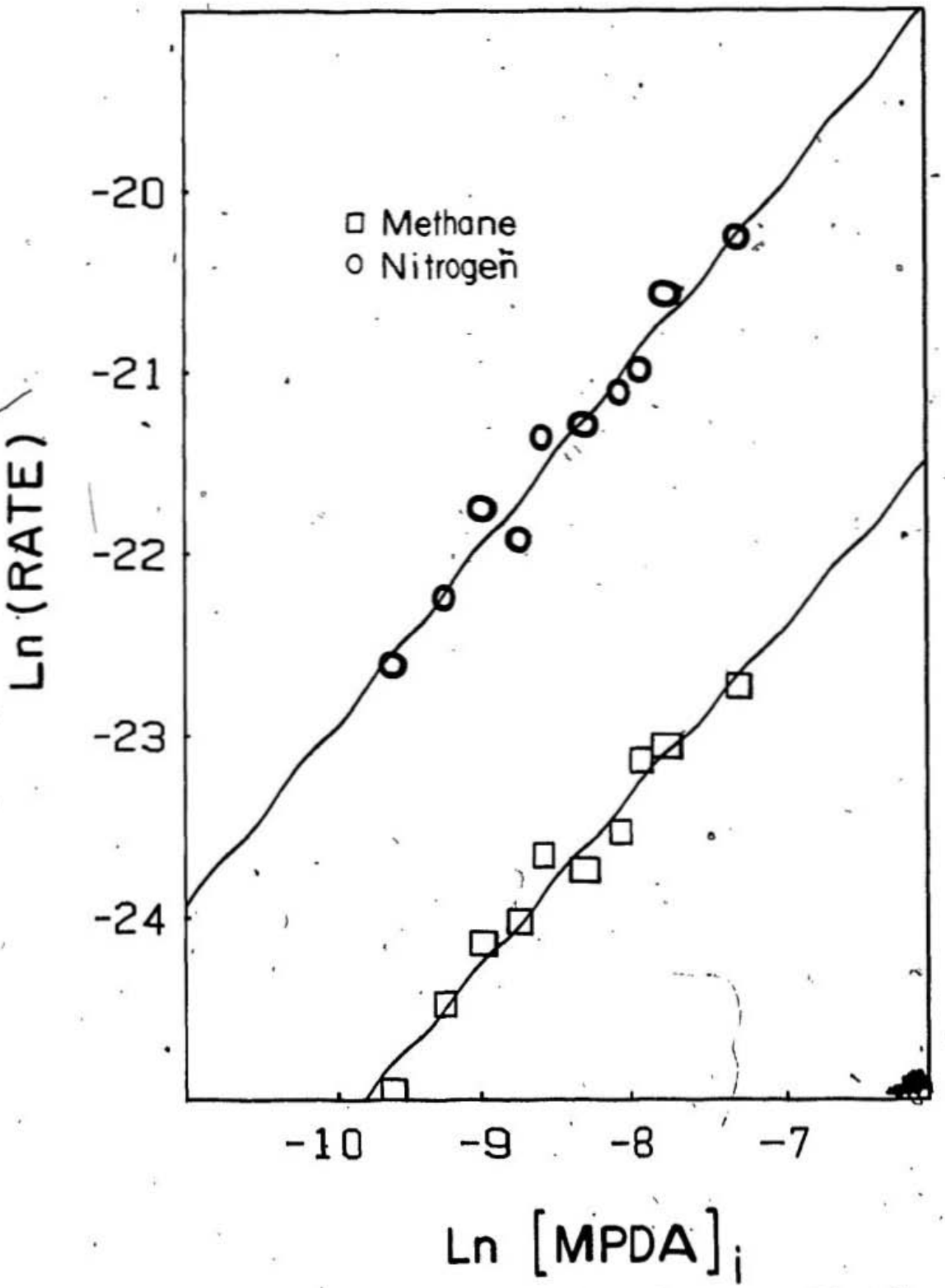


Figure 10. Order plot for nitrogen and methane at 529.4 K in unpacked reaction vessel.

Table 4. Data for the order plots of nitrogen and methane and calculated slopes at 559.0 K in unpacked vessel.

	Order Plots*	
$\ln[MPDA]_i$ †	$\ln[Rate(N_2)]$	$\ln[Rate(CH_4)]$
-9.07	-19.85	-20.84
-8.75	-19.56	-20.16
-8.88	-19.60	-20.29
-9.01	-19.68	-20.46
-8.64	-19.23	-20.39
-8.46	-19.32	-20.27
-8.30	-19.02	-19.97
-8.61	-19.43	-20.47
-8.74	-19.30	-20.33
-8.89	-19.54	-20.52
-9.05	-19.68	-20.73
-9.23	-19.85	-20.87
-9.39	-20.23	-21.32
-9.55	-20.22	-21.22
-10.06	-20.69	-21.95
-7.88	-18.43	-19.33
-8.29	-18.79	-19.98
-7.50	-18.13	-19.00
-7.43	-17.79	-18.88
-7.00	-17.48	-18.63
-6.86	-17.33	-18.48

* Time(s) 1000, Temperature 559.0 K

† 1-Methyl-2-phenyldiazene = MPDA

Slope (Nitrogen) 1.09 ± 0.03

Slope (Methane) 1.08 ± 0.04

Table 5. Data for the order plots of nitrogen and methane and calculated slopes at 529.4 K in unpacked vessel.

	Order Plots*	
$\ln[MPDA]_i$ †	$\ln[Rate(N_2)]$	$\ln[Rate(CH_4)]$
-9.60	-22.61	-24.95
-9.27	-22.24	-24.47
-8.99	-21.75	-24.14
-8.59	-21.36	-23.66
-8.31	-21.29	-23.74
-8.07	-21.11	-23.53
-7.91	-20.99	-23.14
-7.28	-20.26	-22.73
-7.75	-20.57	-23.06
-8.77	-21.92	-24.02

* Time(s) 2000, Temperature 529.4 K

† 1-Methyl-2-phenyldiazene = MPDA

Slope (Nitrogen) 0.99 ± 0.06

Slope (Methane) 0.92 ± 0.06

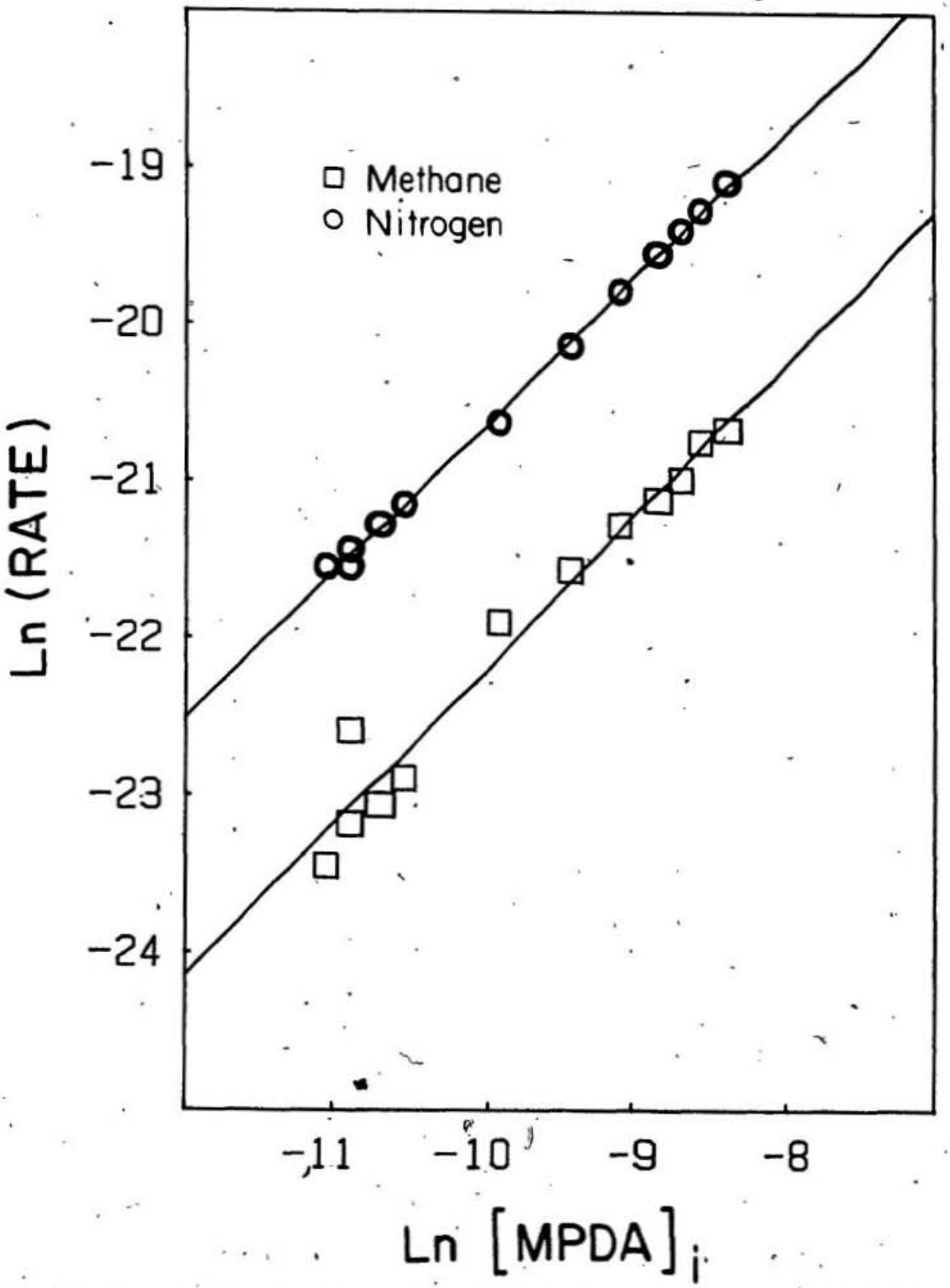


Figure 11. Order plot for nitrogen and methane at 559.0 K in unpacked reaction vessel with propene added.

Table 6. Data for the order plots of nitrogen and methane and the calculated slopes at 559.0 K with propene added in unpacked vessel.

$\ln[MPDA]_i$ †	$\ln[Rate(N_2)]$	$\ln[Rate(CH_4)]$	$k(s^{-1} \times 10^5)(N_2)$
-10.56††	-21.15	-22.89	2.528
-10.71††	-21.28	-23.06	2.603
-10.80††	-21.44	-23.18	2.679
-11.05††	-21.55	-23.45	2.759
-8.37	-19.09	-20.67	2.235
-8.55	-19.27	-20.75	2.211
-8.69	-19.40	-20.99	2.258
-8.84	-19.55	-21.12	2.256
-9.09	-19.79	-21.28	2.278
-9.43	-20.14	-21.57	2.248
-9.93	-20.63	-21.90	2.268
-10.89	-21.55	-22.59	2.364

Time 1000s, Temperature 559.0 K

† 1-Methyl-2-phenyldiazene = MPDA

†† Propene: Diazene ratio was 85.2 to 1 for these runs, all others were in a 9 to 1 ratio.

Slope (Nitrogen) 0.94 ± 0.01

Slope (Methane) 0.98 ± 0.06

It should be noted that the average values of the rate constant for each ratio of propene to 1-methyl-2-phenyldiazene are different. This is also reflected in the order plots for both nitrogen and methane. There does not appear to be a statistical significance to this, however, as the value of the rate constant "k" of the uninhibited runs, within its confidence interval, brackets these two values.

Further study of this effect was made by preparing five additional mixtures of 1-methyl-2-phenyldiazene. These mixtures were equilibrated for about 30 minutes and then pyrolysed, in contrast with the first two mixtures which were equilibrated for twelve hours before pyrolysis. Also, only the first run for each mixture is illustrated in figure 12. There is an obvious inhibition of the rate of nitrogen formation when the initial mixture is used.

In attempting to understand this discrepancy in rate constants between the sets of experiments, mixtures of propene and 1-methyl-2-phenyldiazene were equilibrated for up to forty-eight hours in the 5 L vessel. These mixtures were then condensed through the reaction vessel at ambient temperature to see if any reaction took place in the mixing vessel. But no appreciable yield of nitrogen or of methane could be detected after that length of time.

One possible explanation could be the formation of the *cis* isomer of 1-methyl-2-phenyldiazene in the mixing vessel. If the *cis* isomer decomposes rapidly to produce sufficient nitrogen to balance the inhibiting effect of propene on the *trans* isomer, there would be no measurable effect of adding propene.

It should also be noted that the penultimate propene run† at 559.0 K of the second mixture was carried out to 99.7 percent reaction. With one exception, runs (without propene) after this had large rate constants for nitrogen formation. In some runs they were two to four times that of previous runs at the same temperatures.

---

† 11.0% 1-methyl-2-phenyldiazene

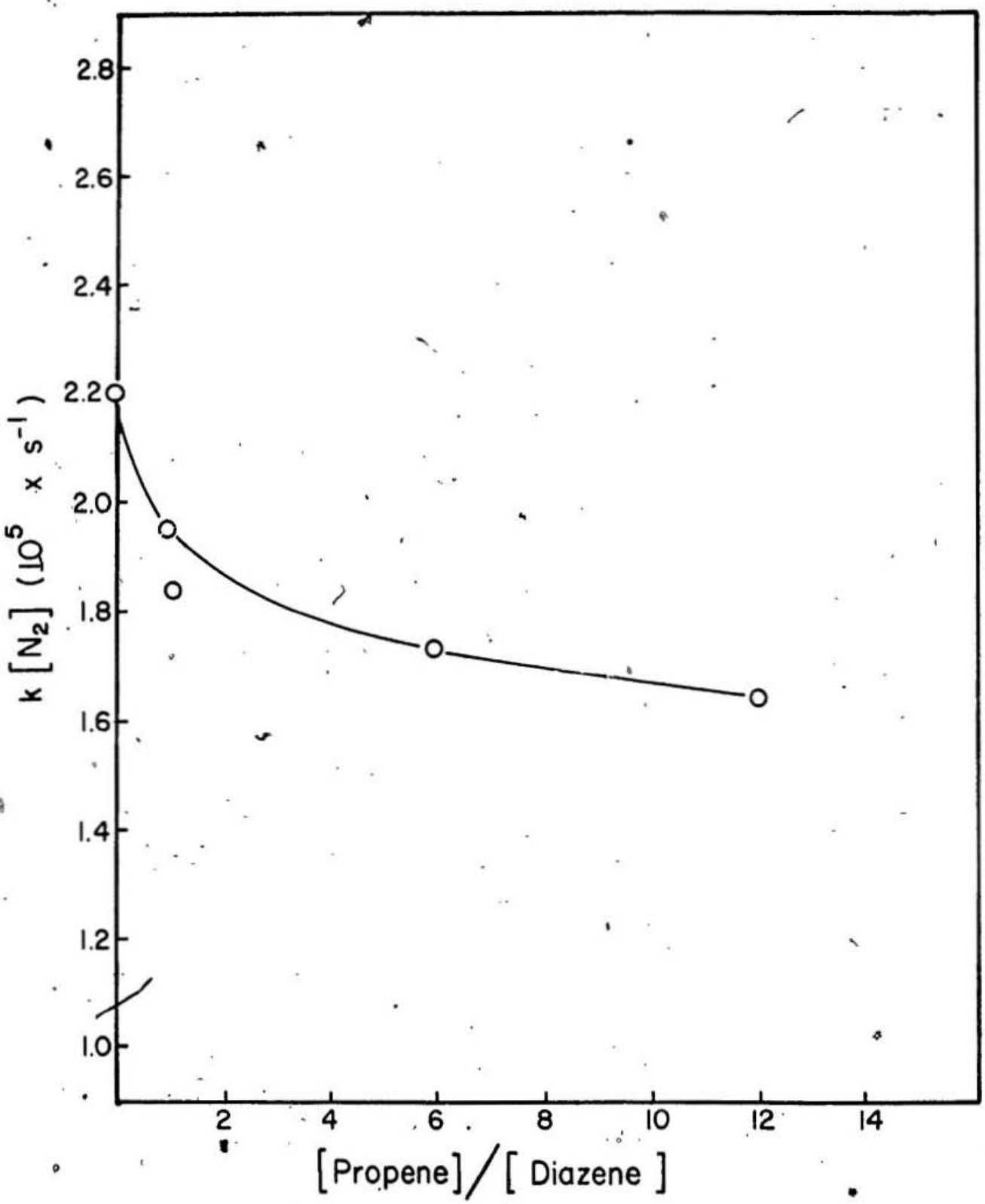


Figure 12. Plot of the rate constant for nitrogen formation versus initial ratio of 1-methyl-2-phenyldiazene to propene at 559.0 K in unpacked reaction vessel.

Also, while the absolute amount of nitrogen was high, the yield of methane was below that of previous runs under identical conditions. This problem persisted for several months, until the reaction vessel was finally replaced by a new, unused, vessel. A possible explanation for this behaviour is found in the discussion section.

A comparison of some normal and erratic runs is given in Table 7.

e. Rate Constant versus Temperature and Arrhenius Parameters

To obtain the best possible values for the Arrhenius parameters each value of the rate constant, k, and the temperature, T, was fitted to $k = A\ e^{-Ea/RT}$ by non-linear regression analysis.

Figure 13 shows the data fitted to the exponential curve while figure 14 shows the more common plot of ln k *versus* 1/T, using the average values of ln k for each temperature. Table 8 is a listing of the data for the exponential fit and the calculated Arrhenius parameters.

3. Packed Vessel

As with the unpacked vessel two fractions of products were collected. Those products which passed through a liquid nitrogen trap and those which condensed. The non-condensable fraction, nitrogen and methane, were analysed as described for the unpacked vessel.

For the condensed fraction, using the procedure of analysis as outlined in the experimental section, it was found after thirty runs that a quantity of material had remained in the copper tubing. This indicated that some of the material had not been swept onto the gas chromatograph and, because it was not known how much of the products had been absorbed in the retained material, the method of analysis was abandoned.

As with the unpacked vessel an Arrhenius plot was made of the data using an

Table 7. Example of Normal and Erratic Runs at 529.4 K without Propene.

Run No.	k x 10^6 (s^{-1})(N_2)	k x 10^7 (s^{-1})(CH_4)
121	2.24	3.62
122	2.34	3.84
123	2.90	4.09
124	2.89	4.14
126	2.33	3.64
174*	3.20	2.42
175*	3.36	2.42
177*	3.05	3.01
178*	4.14	1.70
179*†	7.69	1.84
180*†	6.56	1.53

* After the complete (99.7%) reaction with propene.

† Packed vessel. All others, unpacked vessel.

Table 8. Data for the exponential fit of the rate of nitrogen formation *versus* temperature with the calculated activation energy and pre-exponential factor in unpacked reaction vessel.

Temp(K)	$k(s^{-1} \times 10^5)$	Temp(K)	$k(s^{-1} \times 10^5)$	Temp(K)	$k(s^{-1} \times 10^5)$
559.0	2.136	559.0	2.872	529.4	0.2025
559.0	2.053	559.0	2.401	529.4	0.1945
559.0	2.259	559.0	2.101	529.4	0.2011
559.0	2.381	559.0	1.924	519.4	0.1047
559.0	2.528	559.0	2.291	519.4	0.08807
559.0	1.943	559.0	1.944	519.4	0.08786
559.0	2.233	559.0	2.130	539.4	0.6107
559.0	2.027	559.0	2.296	539.4	0.4805
559.0	2.613	559.0	2.714	539.4	0.5289
559.0	2.401	559.0	2.208	539.4	0.5094
559.0	2.439	559.0	2.308	549.2	1.129
559.0	2.459	529.4	0.2239	549.2	1.271
559.0	1.981	529.4	0.2343	549.2	1.074
559.0	2.327	529.4	0.2001	549.2	1.088
559.0	2.425	529.4	0.2889	549.2	1.161
559.0	2.629	529.4	0.2333	549.2	1.136
559.0	2.752	529.4	0.2198	568.8	4.759
559.0	2.435	529.4	0.2111	568.8	4.891
559.0	2.192	529.4	0.2313	568.8	4.388
559.0	2.759	529.4	0.2728	559.0	2.627
559.0	2.169	529.4	0.1964	559.0	2.783
559.0	2.954	529.4	0.1957	559.0	2.828
559.0	2.732	529.4	0.1953		
559.0	2.205	529.4	0.1582		
559.0	2.337	529.4	0.2084		
559.0	2.369	529.4	0.2095		

$A = 4.22 \times 10^{13} \pm 1.68 \times 10^{13}\ s^{-1}$

$Ea = 1.95 \times 10^{5} \pm 1.83 \times 10^{3}\ J\ mol^{-1}$

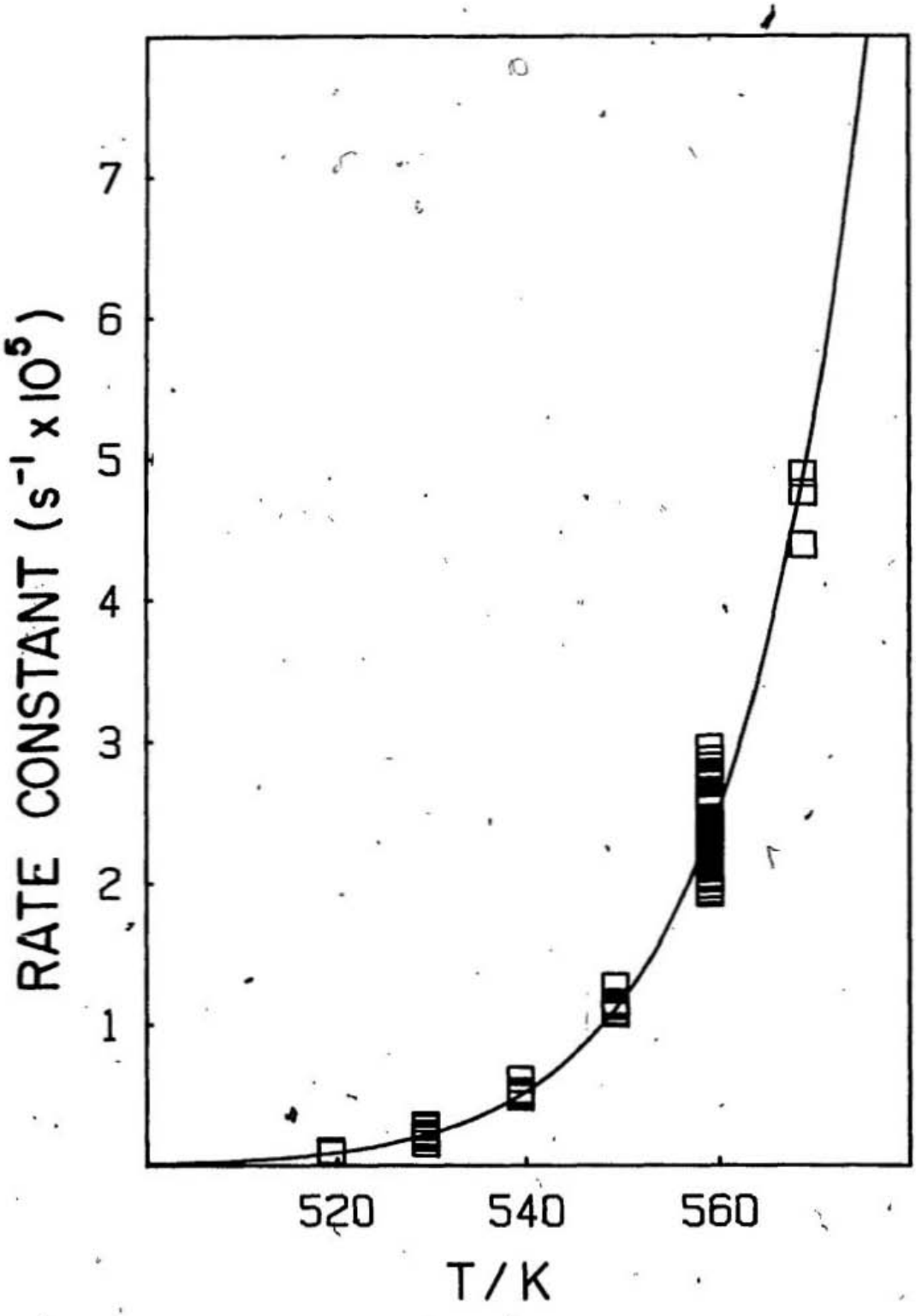


Figure 13. Plot of the rate constant for nitrogen formation versus temperature in unpacked reaction vessel.

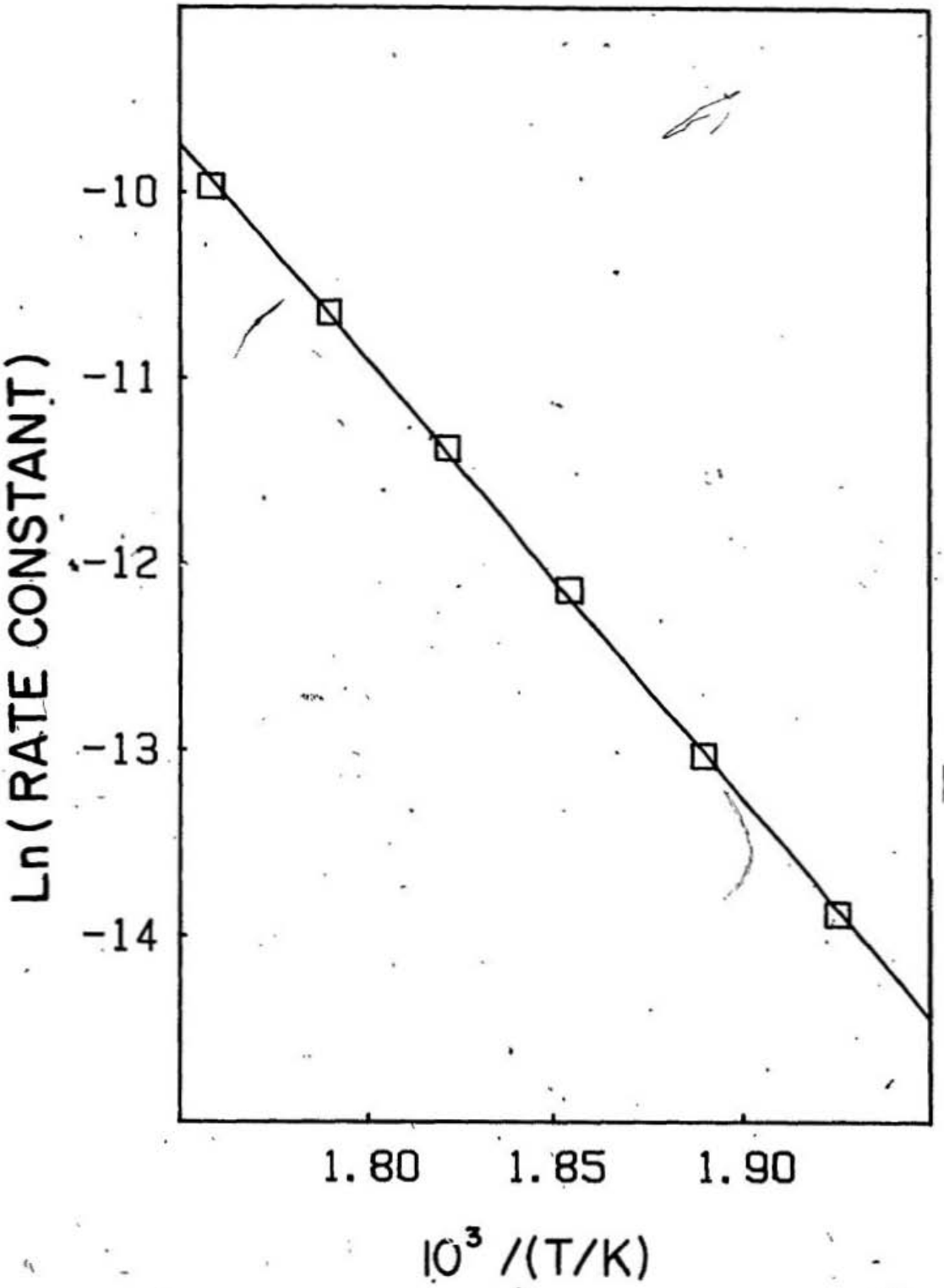


Figure 14. Arrhenius plot for nitrogen in unpacked reaction vessel.

exponential curve and the more common ln k *versus* 1/T straight line fit. As before, non-linear regression analysis was used for each value of the rate constant k and the temperature T to give the best possible Arrhenius parameters.

Figure 15 shows the data fitted to the exponential curve and Table 9 contains the listing of the data with the calculated Arrhenius parameters. Figure 16 is the plot of ln k *versus* 1/T for the average values of ln k for each temperature.

Definite conclusions from the packed vessel experiments are difficult to reach, because there was a number of mitigating factors. First, the vessel itself had previously been used for surface/volume effects with azobenzene and the surface may have been modified. Second, the 1-methyl-2-phenyldiazene used for these experiments contained 0.43% aniline as the gas chromatographic procedure had not yet been developed for purification. Finally, the viton sealed valves in the original vacuum line may have leaked helium into the gas burette during collection giving higher than expected gas volumes.

For purposes of comparison Table 10 lists the average rate constants for each temperature in both vessels. Except for 559.0 K the table shows that the rate constant for nitrogen formation is larger for the packed *versus* the unpacked reaction vessel. But the set of experiments at 559.0 K were the first completed and they agree with those in the unpacked vessel. Based on the accelerated rate constants for nitrogen formation that were obtained when the packed vessel was used after the propene experiments it would appear that it also had a surface coating which would make the results suspect.

After due consideration, not withstanding the comments above, for the purpose of discussion it was assumed that, as pyrolysis reactions of azomethane and azobenzene are claimed to be homogeneous (4,5), reactions affecting the rate of nitrogen formation are essentially homogeneous. Also, under certain (obscure) circumstances the surface affects the rate of nitrogen formation.

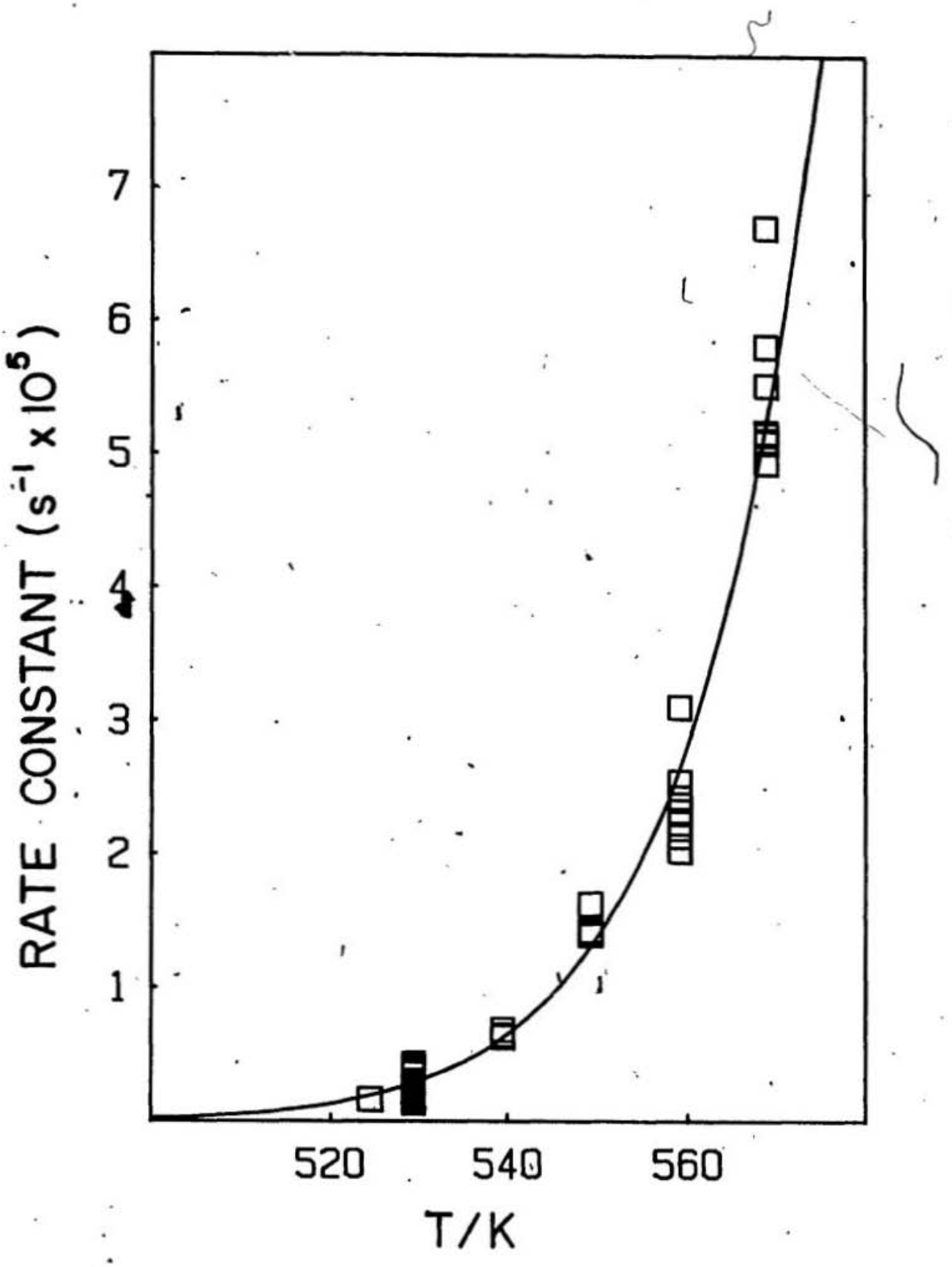


Figure 15. Plot of the rate constant for nitrogen formation versus temperature in packed reaction vessel.

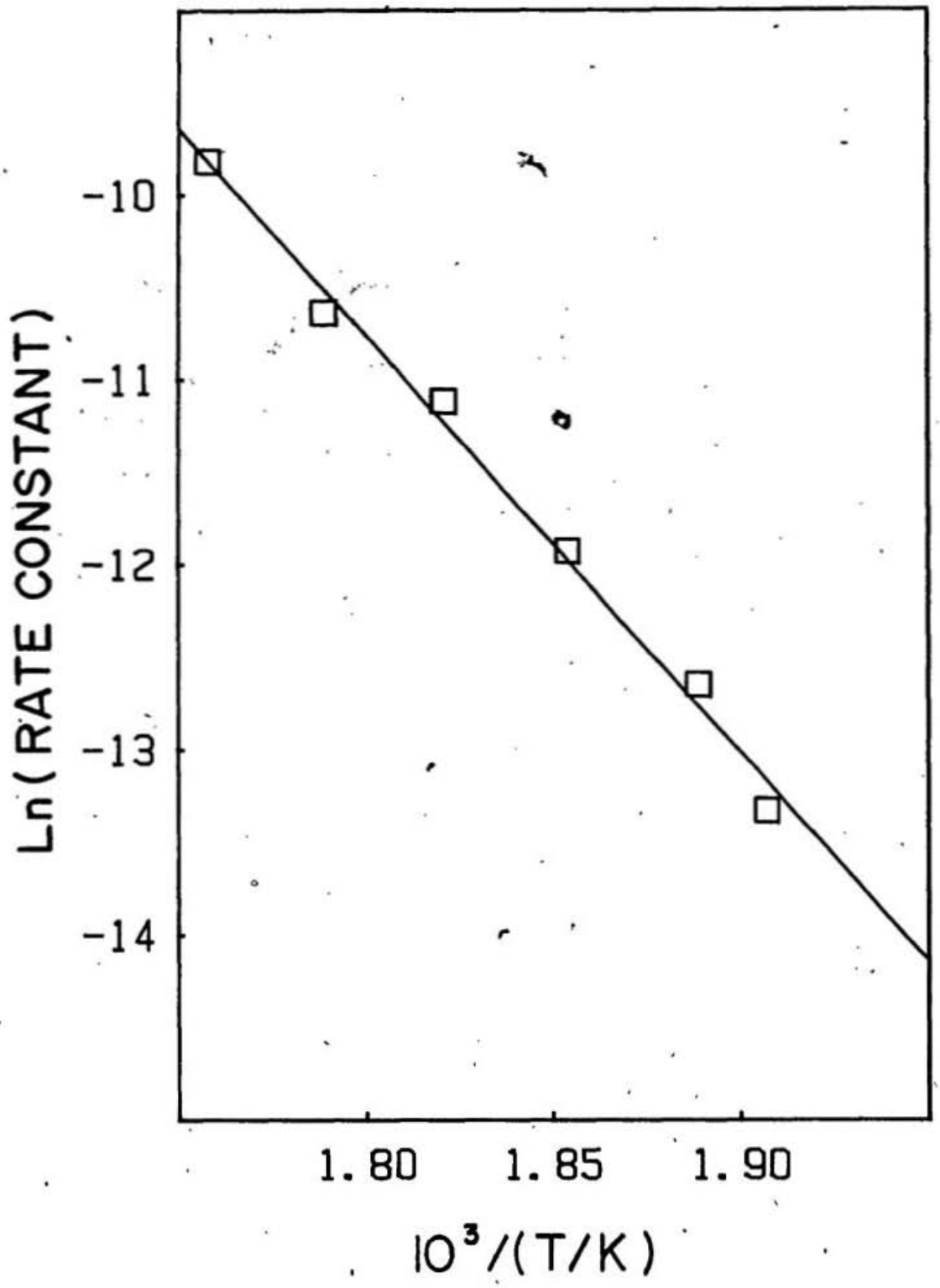


Figure 16. Arrhenius plot for nitrogen in packed reaction vessel.

Table 9. Data for the exponential fit of the rate of nitrogen formation versus temperature with the calculated activation energy and pre-exponential factor in packed reaction vessel.

Temp(K)	$k(s^{-1} \times 10^5)$	Temp(K)	$k(s^{-1} \times 10^5)$
559.0	2.026	539.4	0.6334
559.0	2.136	529.4	0.2412
559.0	2.234	529.4	0.2385
559.0	2.426	529.4	0.3412
559.0	2.545	529.4	0.2153
559.0	3.101	529.4	0.3280
559.0	2.323	529.4	0.2950
568.8	5.519	529.4	0.2882
568.8	5.163	529.4	0.2564
568.8	5.811	529.4	0.2529
568.8	5.104	529.4	0.3506
568.8	6.704	529.4	0.4162
568.8	4.935	529.4	0.4851
568.8	5.147	529.4	0.3035
568.8	5.088	529.4	0.2741
524.5	0.1626	529.4	0.3135
549.2	1.428	529.4	0.3506
549.2	1.396	529.4	0.4030
549.2	1.628	529.4	0.3066
539.4	0.6860	529.4	0.4369
539.4	0.6478	529.4	0.3330

$A = 9.12 \times 10^{11} \pm 3.61 \times 10^{11}\ s^{-1}$

$Ea = 1.77 \times 10^5 \pm 1.84 \times 10^3\ J\ mol^{-1}$

Table 10. Mean rate constants for nitrogen formation in the packed and unpacked reaction vessels.

Temp(K)	No. of Runs	Unpacked $k(s^{-1} \times 10^5)$	No. of Runs	Packed $k(s^{-1} \times 10^5)$
519.4	3	0.0938 ± 0.0077		
524.5			1	0.1626
529.4	18	0.2204 ± 0.0335	20	0.3224 ± 0.0700
539.4	3	0.5093 ± 0.0161	3	0.6557 ± 0.0222
549.2	6	1.143 ± 0.064	3	1.484 ± 0.103
559.0	40	2.380 ± 0.275	7	2.340 ± 0.329
568.8	3	4.679 ± 0.213	8	5.434 ± 0.547

IV Discussion

This discussion is intended to account for the following observations:

(1) The order for nitrogen formation is 1.04 ± 0.04.

(2) The activation energy, Ea, is less than that of azomethane or azobenzene.

(3) The pre-exponential factor, A, is two to three orders of magnitude less than that expected of a simple fission reaction.

(4) The rate of nitrogen formation is decreased by the addition of propene.

(5) A variety of products is formed during pyrolysis.

1. Interpretation of Data

There are, possibly, three interpretations of the data for the pyrolysis of 1-methyl-2-phenyldiazene:

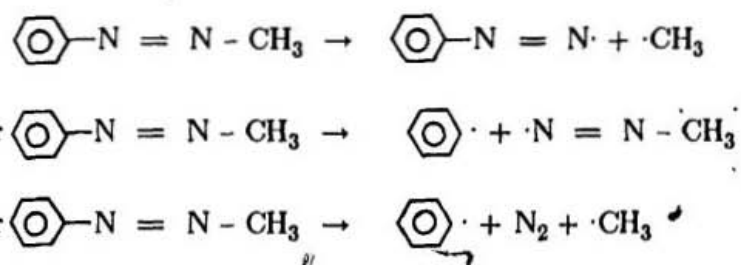
(1) Rate controlling elementary fission.

(2) Rate controlling isomerization followed by pyrolysis.

(3) Chain reaction.

2. Rate Controlling Elementary Fission

Decomposition of 1-methyl-2-phenyldiazene, with no contribution from a chain reaction, could take place through reactions such as:



There are two major arguments against using these as rate determining steps. First, propene should have no effect on the rate of nitrogen formation, in contradic-

tion with the observations. Second, the 1-methyl-2-phenyldiazene would be expected to pass through a "loose" transition state. Such a loose transition state leads to a high pre-exponential factor, normally of 10^{16} - 10^{17} s^{-1} (36), which is much higher than the experimental value. Of course these arguments do not exclude a contribution of such reactions.

3. Rate Controlling Isomerization

The second possibility is envisaged as *trans* to *cis* isomerization of 1-methyl-2-phenyldiazene, which would be rate controlling, followed by pyrolysis. This possibility was seriously considered when the first results using propene, which indicated the absence of inhibition, were obtained. Low values of the pre-exponential factor and the absence of inhibition are expected of isomerization. To reinforce this view, it is known that *cis*-diazenes are reactive (3). In addition a new study of 2,2'-di(isopropyl)-diazene has been published in which a low value of the pre-exponential factor was claimed (16). However, the subsequent results using propene eliminated isomerization as the exclusive mechanism.

4. Chain Reaction

a. Simple Mechanism

The effect of propene seems best interpreted as due to some contribution of a chain mechanism. In addition, the fact that the pre-exponential factor is so low, and that the activation energy is below that of the assumed elementary fission reactions of both azomethane and azobenzene, support this view. Therefore, most of the subsequent discussion is concerned with a chain mechanism.

To facilitate this discussion the proposed mechanism is first presented in its simpliest terms and then expanded upon to accommodate further discussion.

Shown below is a simple mechanism designed to explain certain observations which have been made. The diazene is considered to be symmetrical in this initial

part of the discussion, in the interests of clarity.

[1] $D \rightarrow 2R_1\cdot + N_2$

[2] $R_1\cdot + D \rightarrow P + R_2\cdot$

[3] $R_2\cdot \rightarrow N_2 + R_1\cdot + X:$

[4] $R_1\cdot + D \rightarrow R_3\cdot$

[5] $R_1\cdot + R_2\cdot \rightarrow R_1 - R_2$

[6] $R_3\cdot + D \rightarrow P_1 + R_2\cdot$

[7] $P_1 \rightarrow R_4\cdot + R_5\cdot$

[8] $R_4\cdot + D \rightarrow A_4 + R_2\cdot$

[9] $R_5\cdot + D \rightarrow A_5 + R_2\cdot$

The symbols in the above equations have the following meaning:

D diazene

$R_1\cdot$ hydrocarbon radical

P hydrocarbon product

P_1 a hydrazine

$R_2\cdot$ diazene radical, $R_1 - N = N - R_1$

$R_3\cdot$ hydrazine radical, $R_1 - \underset{R_1}{N} - N - R_1$

$R_4\cdot$, $R_5\cdot$ amine radicals, $R_1 - \underset{R_1}{N}\cdot$, $\underset{H}{N} - R_1$

A_4, A_5 amines, $R_1 - \underset{H}{N} - R_1$, $H - \underset{H}{N} - R_1$

$R_1 - R_2$ a new diazene

X: diradicals

Reactions [1] and [2] are standard reactions which have often been invoked (4,7,45) to explain the formation of the major products, nitrogen and hydrocarbons. The question of whether reaction [1] is a one or two step process was the original incentive for this study, and will be considered later.

One observation, already mentioned, is that propene inhibits the rate of nitrogen formation, at least when pyrolysis immediately follows mixing of 1-methyl-2-phenyldiazene and propene. As propene has been shown to interfere with radical chain reactions (5,6), such behavior would imply that there is a source of nitrogen in addition to reaction [1]. Reaction [3] or one similar to it has been used (5) to represent this second source of nitrogen. Reaction [3] would also be the source of the chain propagating radical, $R_1\cdot$, and thus the rate of nitrogen formation would be decreased if $R_1\cdot$ reacted with propene.

Reaction [5], a termination reaction in which two different radicals combine, was used instead of the conventional reaction, [10].

[10] $\quad R_1\cdot + R_1\cdot \rightarrow R_1 - R_1$

The reason for doing this is given in the following paragraphs.

Recall that nitrogen formation is first order, or nearly so, with respect to the initial concentration of 1-methyl-2-phenyldiazene. Therefore, the steady state approximation for the rate of nitrogen formation also should give a rate equation which is first order with respect to the diazene.

Considering the mechanism in its simplest terms by omitting amine formation, and using reaction [10] as the termination reaction, the sequence would be

[1] $\quad D \rightarrow 2R_1\cdot + N_2$

[2] $\quad R_1\cdot + D \rightarrow P + R_2\cdot$

[3] $\quad R_2\cdot \rightarrow N_2 + R_1\cdot + X$:

[10] $R_1\cdot + R_1\cdot \rightarrow R_1 - R_1$

D, $R_1\cdot$, $R_2\cdot$ and P were defined above and $R_1 - R_1$ is a hydrocarbon product.

By using the stationary state method one obtains the following rate equations for the chain contribution to the rate of nitrogen formation, depending on the order of reactions [1] and [10].

Reaction	Order	Rate Equation for N_2 Formation Due to the Reaction Chain
[1] [10]	1 2	$\frac{d[N_2]}{dt} = k_2\left(\frac{k_1}{k_{10}}\right)^{1/2}[D]^{3/2}$
[1] [10]	1 3	$\frac{d[N_2]}{dt} = k_2\left(\frac{k_1}{k_{10}}\right)^{1/2}[D]^{1}$
[1] [10]	2 2	$\frac{d[N_2]}{dt} = k_2\left(\frac{k_1}{k_{10}}\right)^{1/2}[D]^{2}$
[1] [10]	2 3	$\frac{d[N_2]}{dt} = k_2\left(\frac{k_1}{k_{10}}\right)^{1/2}[D]^{3/2}$

As shown above, the orders of reaction [1] and [10] would have to be one and three respectively to give a first order rate of nitrogen formation with respect to the diazene.

But MacPherson (33) has shown that the rate constant for methyl radical recombination in the pressure and temperature range of this study is in its fall off region and therefore should be between second and third order and would also show strong pressure dependence.

In the case of 1-methyl-2-phenyldiazene the other possible termination reactions are

[14] $CH_3\cdot + \cdot C_6H_5 \rightarrow C_6H_5CH_3$

$$[15] \quad \cdot C_6H_5 + \cdot C_6H_5 \rightarrow C_{12}H_{10}.$$

Both would be second order.

If the data assembled by Holbrook (34) are used for guidance, the rate of decomposition of a molecule of the complexity of 1-methyl-2-phenyldiazene should be first order in the pressure range of this study. Therefore this implies that the combination of the initially formed radicals, $\cdot CH_3$ and $\cdot C_6H_5$, should not be the termination step of this mechanism.

b. Simple Mechanism with $R_1\cdot$, $R_2\cdot$ Termination

If however the termination reaction was:

$$[5] \quad R_1\cdot + R_2\cdot \rightarrow R_1 - R_2,$$

instead of reaction [10], where $R_1\cdot$ and $R_2\cdot$ represent a hydrocarbon and a diazene radical respectively a first order chain mechanism is obtained.†

The stationary state treatment is greatly simplified if the long chain approximation is made at the beginning, and the termination reaction is omitted from the rate equation for $R_2\cdot$. Then, using Mulcahy's procedure (32), the rate equations are written in the following way.

(1) The rate of initiation is equal to the rate of termination;

$$[1] \quad 2k_1[D] = k_5[R_1][R_2], \text{ and}$$

(2) the differential equation for $[R_2]$ becomes,

$$[2] \quad \frac{d[R_2]}{dt} = k_2[R_1][D] - k_3[R_2] + k_6[R_3][D] + k_8[R_4][D] + k_9[R_5][D]$$

† An example is described by K.J. Laidler in Chemical Kinetics. 3rd ed. Harper and Row, New York, 1987, p. 308.

$$[11] \qquad [R_2] = \left[\frac{2k_1k_2}{k_3k_5} + \frac{6k_1k_4}{k_3k_5}\right]^{\frac{1}{2}}[D]$$

and substitution of [11] into [3], and rearranging gives finally

$$[12] \qquad \frac{d[N_2]}{dt} = \left[k_1 + \left(\frac{2k_1k_2k_3}{k_5} + \frac{6k_1k_3k_4}{k_5}\right)^{\frac{1}{2}}\right][D].$$

Equation [12] is consistent with what was found experimentally in the sense that the rate of nitrogen formation is first order with respect to the initial concentration of 1-methyl-2-phenyldiazene. Therefore, the termination reaction apparently involves the recombination of initially formed radical and the diazene radical.

c. Complete Mechanism

The simple mechanisms were based on a symmetrical diazene and were used to show that certain features of the reaction could be explained. For a more complete discussion the following mechanism is proposed for the pyrolysis of the asymmetrical 1-methyl-2-phenyldiazene.

[16] $\bigcirc\!\!-N=N-CH_3 \rightarrow N_2 + \cdot CH_3 + \cdot C_6H_5$

[17] $\cdot CH_3 + \bigcirc\!\!-N=N-CH_3 \rightarrow CH_4 + \cdot CH_2-N=N-\bigcirc$

[18] $\cdot CH_3 + \bigcirc\!\!-N=N-CH_3 \rightarrow CH_4 + CH_3-N=N-\bigcirc\cdot$

[19] $\cdot\bigcirc + \bigcirc\!\!-N=N-CH_3 \rightarrow \bigcirc + \cdot CH_2-N=N-\bigcirc$

[20] $\cdot\bigcirc + \bigcirc\!\!-N=N-CH_3 \rightarrow \bigcirc + CH_3-N=N-\bigcirc\cdot$

[21] $\cdot CH_2-N=N-\bigcirc \rightarrow N_2 + :CH_2 + \cdot\bigcirc$

(3) The other rate equations would be:

$$[3] \quad \frac{d[N_2]}{dt} = k_1[D] + k_3[R_2]$$

$$[4] \quad \frac{d[R_3]}{dt} = k_4[R_1][D] - k_6[R_3][D]$$

$$[5] \quad \frac{d[P_1]}{dt} = k_6[R_3][D] - k_7[P_1]$$

$$[6] \quad \frac{d[R_4]}{dt} = k_7[P_1] - k_8[R_4][D]$$

$$[7] \quad \frac{d[R_5]}{dt} = k_7[P_1] - k_9[R_5][D]$$

Using the Steady State Approximation for [4], [5], [6] and [7] one obtains:

$$k_4[R_1][D] = k_6[R_3][D]$$

and

$$k_6[R_3][D] = k_7[P_1] = k_8[R_4][D] = k_9[R_5][D]$$

Substitution of $k_4[R_1][D]$ into [2] one obtains:

$$[8] \quad \frac{d[R_2]}{dt} = 0 = k_2[R_1][D] - k_3[R_2] + 3k_4[R_1][D].$$

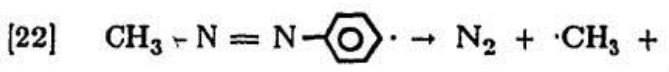
Then rearrangement of [1] into [9]

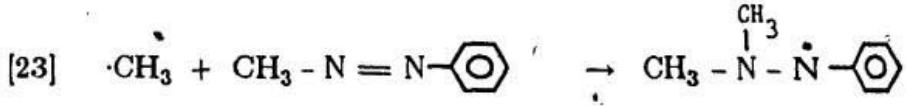
$$[9] \quad [R_1] = \frac{2k_1[D]}{k_5[R_2]}$$

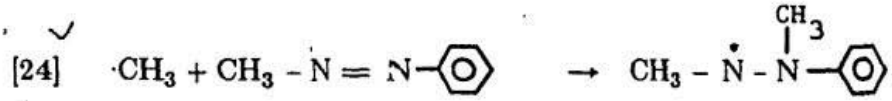
by substitution of [9] into [8], then multiplying through by $[R_2]$, gives [10].

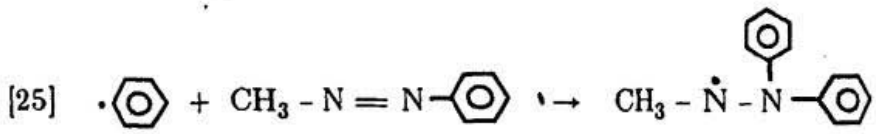
$$[10] \quad \frac{2k_1k_2}{k_5}[D]^2 - [k_3][R_2]^2 + \frac{6k_1k_4}{k_5}[D]^2 = 0$$

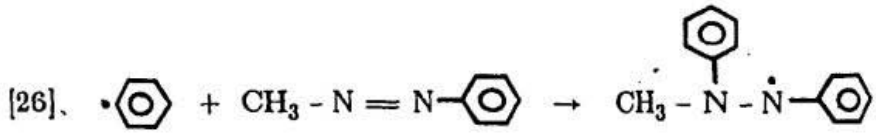
Solving [10] for $[R_2]$, gives [11].

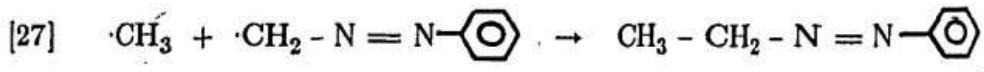
[22] 

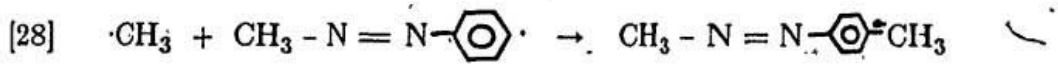
[23] 

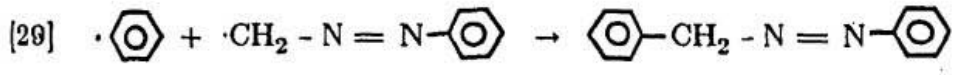
[24] 

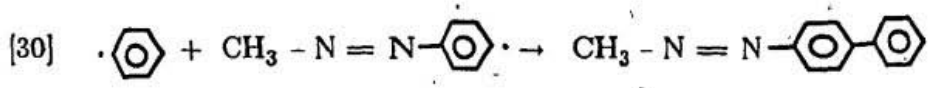
[25] 

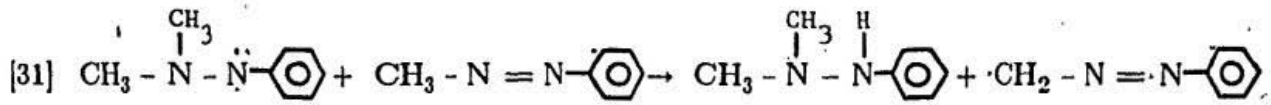
[26] 

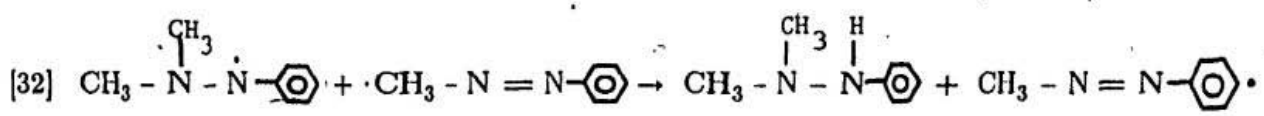
[27] 

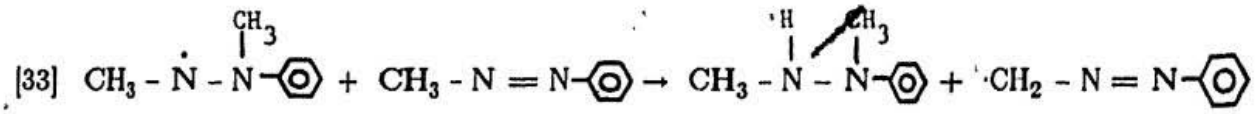
[28] 

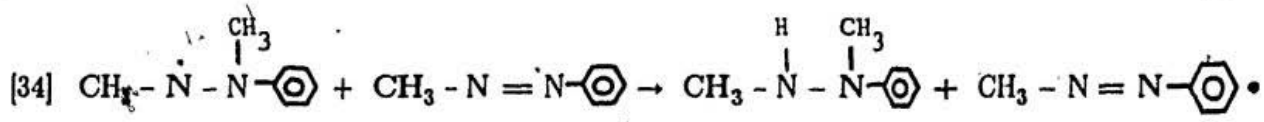
[29] 

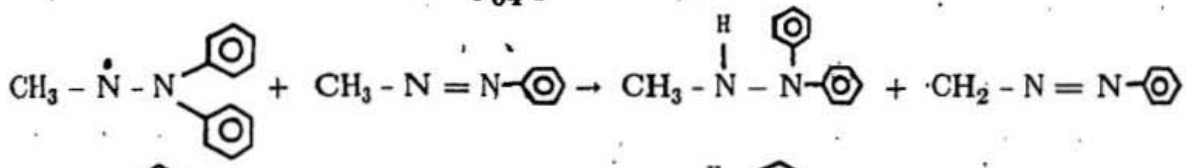
[30] 

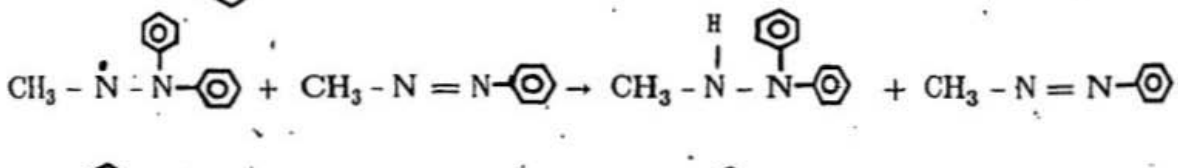
[31] 

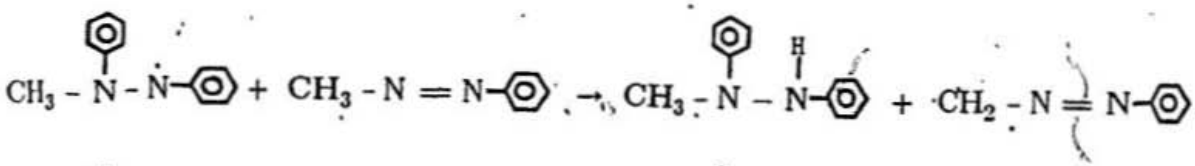
[32] 

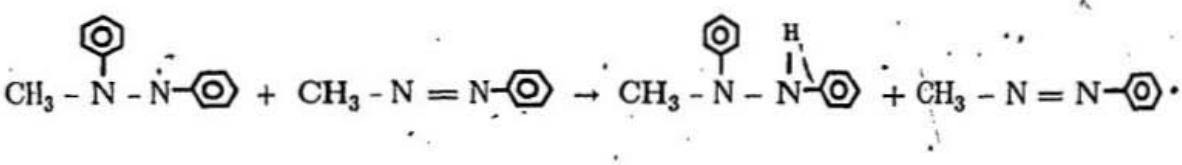
[33] 

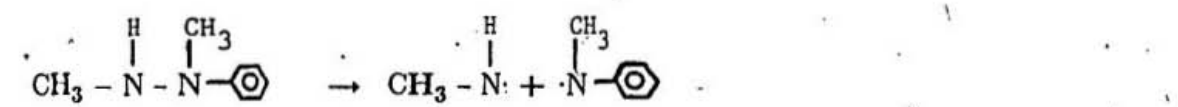
[34] 

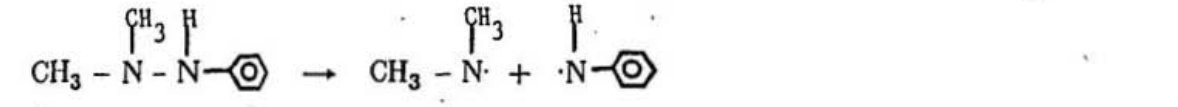
[35] 

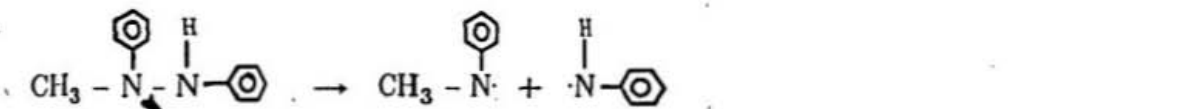
[36] 

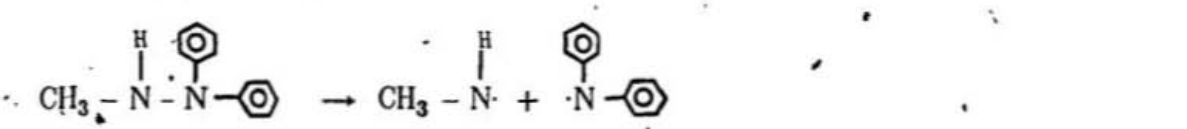
[37] 

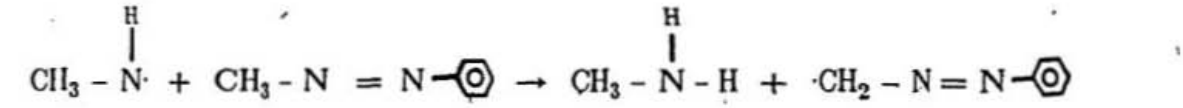
[38] 

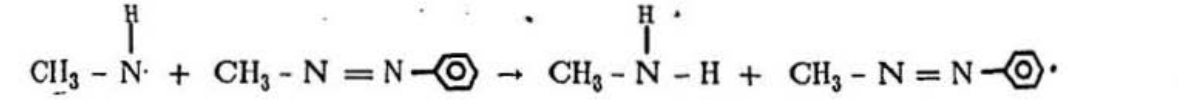
[39] 

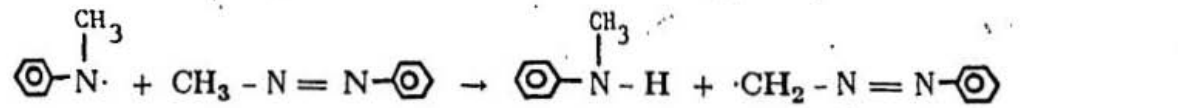
[40] 

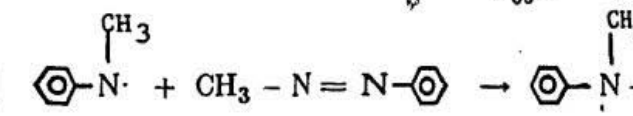
[41] 

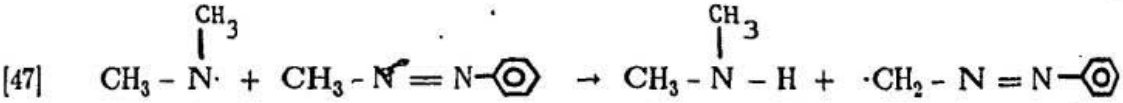
[42] 

[43] 

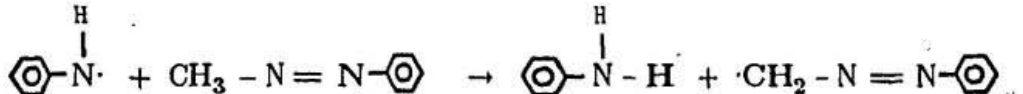
[44] 

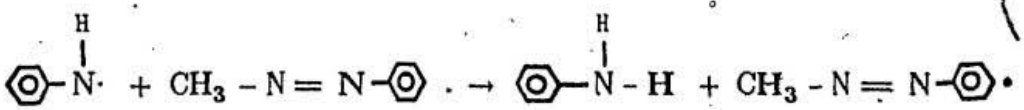
[45] 

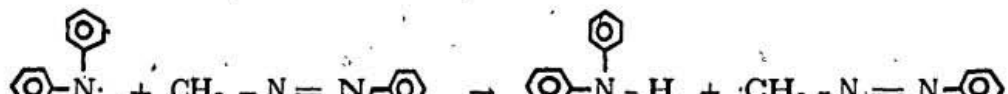
[46] 

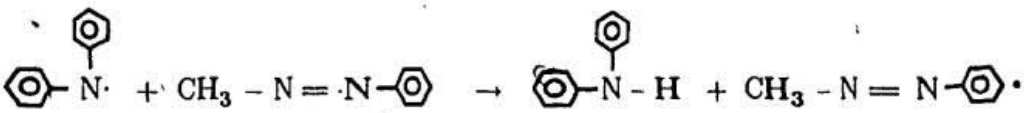
[47] 

[48] 

[49] 

[50] 

[51] 

[52] 

There are two important features in the above mechanism which distinguish it from the simple ones. One is the fact that, because the diazene is not symmetrical, there are four abstraction and four termination reactions for each one in the simple mechanism. The other is the increase in number of the reactions which could be referred to as the "amine" chain. These are reactions [31] to [52]. Such reactions concern the fate of the hydrazine radicals, (reactions [23] to [26]), which are formed when $\cdot CH_3$ or  adds across the nitrogen double bond. With subsequent hydrogen abstraction from 1-methyl-2-phenyldiazene, (reactions [31] to [38]), they lead to four possible hydrazines.

During this study, in contrast with previous ones (5,7,45), no hydrazines were

found among the products of decomposition. This can be understood in terms of the nature of the possible hydrazines formed. All would be substituted phenylhydrazines and the rate constant for decomposition of phenylhydrazine itself in toluene is 1.5 x 10^{-4} s^{-1} at 559 K (42) which is ten times the rate constant for decomposition of 1-methyl-2-phenyldiazene at that temperature. Therefore reactions [39] to [42] were included to show decomposition of the various hydrazines which would be formed. Hydrogen abstraction by these radicals from 1-methyl-2-phenyldiazene will give a series of amines, as well as two kinds of diazene radicals, in reactions [43] to [52].

The presence of amines, as well as the absence of hydrazines, was indeed observed. However, only two of the five possible amines, aniline and N-methylaniline, were detected. Of course, the others may have been unresolved or undetected on the OV-17 or DB-1 columns. Excluding that possibility it seems that two interpretations are apparent. First, N-methyl-N-phenyl-N'-phenylhydrazine is the only hydrazine formed in appreciable yield, and it reacts to give the observed amines, as in reactions [41], [46] and [49]. Second, all of the possible hydrazines are formed and only N-methyl-N-phenyl-N'-phenylhydrazine produces amines, while the other hydrazines react and produce undetected products, or do not react and were not detected.

d. Speculation on the Formation and Reactions of Diradicals

Reactions [21] and [22] represent two of the main features of this mechanism. One feature is the production of nitrogen as part of the chain mechanism and the other is that they are the chain propagating steps. Both of these points were discussed in connection with the simple mechanism, and references were given. The justification for writing these reactions is that nitrogen does appear to be formed by a chain reaction as well as, presumably, reaction [16]. What was not commented on before was the fate of the possible radicals formed, methylene and benzyne. Two of the possible reactions of these radicals would be insertion into or addition to 1-

methyl-2-phenyldiazene, as it is the most abundant species present.

i. Addition

Addition reactions of methylene and benzyne* would produce, possibly, four other diradicals, as shown in reactions [53] to [56].

[53] $:CH_2 + CH_3-N=N-C_6H_5 \rightarrow CH_3-N(\cdot CH_2)-N-C_6H_5$

[54] $:CH_2 + CH_3-N=N-C_6H_5 \rightarrow CH_3-N(\cdot CH_2)-N\cdot-C_6H_5$

[55] $C_6H_5\cdot + CH_3-N=N-C_6H_5 \rightarrow CH_3-N\cdot-N(C_6H_5)-C_6H_5$

[56] $C_6H_5\cdot + CH_3-N=N-C_6H_5 \rightarrow CH_3-N(C_6H_5)-N\cdot-C_6H_5$

Following Forst's (7) example, it is assumed that each of these new radicals could do one of two things. Rearrangement would give more complex diazenes. The products would be the same as those of insertion reactions, to be discussed below. Alternatively they could react with the 1-methyl-2-phenyldiazene to abstract hydrogen, as in reactions [57] to [60].†

[57] $CH_3-N\cdot-N(\cdot CH_2)-C_6H_5 + CH_3-N=N-C_6H_5 \rightarrow CH_3-N\cdot-N(CH_3)-C_6H_5 + \cdot CH_2-N=N-C_6H_5$

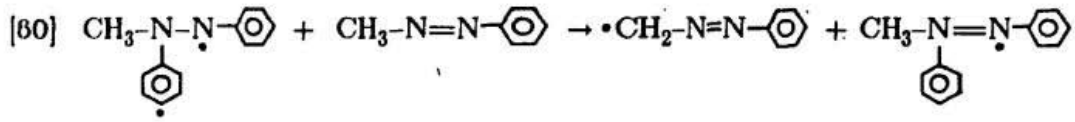
[58] $CH_3-N(\cdot CH_2)-N\cdot-C_6H_5 + CH_3-N=N-C_6H_5 \rightarrow CH_3-N(CH_3)-N\cdot-C_6H_5 + CH_3-N=N-C_6H_5\cdot$

[59] $CH_3-N\cdot-N(C_6H_5)-C_6H_5\cdot + CH_3-N=N-C_6H_5 \rightarrow \cdot CH_2-N=N-C_6H_5 + CH_3-N\cdot-N(C_6H_5)-C_6H_5$

---

* *p*-benzyne is shown as a example. For a discussion of methylene and benzyne, please refer to the book Reactive Molecules by Curt Wentrup, John Wiley and Sons, Toronto, 1984.

† Only four of the eight possible abstraction reactions shown.

[60] 

The radicals are the same ones which are formed in reactions [23] to [26]. Therefore no changes in order of reaction or nature of the products is expected.

ii. Insertion

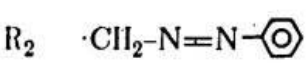
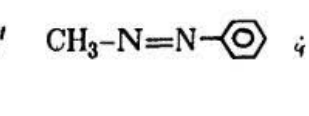
The methylene and benzyne radicals, however, insert quite readily (35). It is assumed that insertion into diazenes is also possible, as suggested by Chang and Rice (43). We also assume that such reactions are possible, and that new diazenes may be formed in this way.

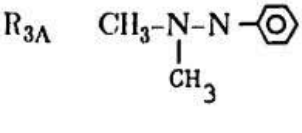
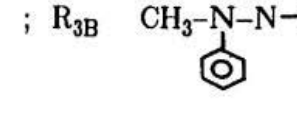
e. Rate Equation for the Complete Mechanism

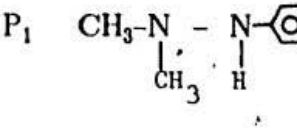
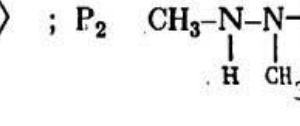
No mention has been made so far that, in the chain contribution to the proposed complete mechanism of nitrogen formation, the order should be one with respect to the initial concentration of 1-methyl-2-phenyldiazene. To show that it is so, one has to use the same procedure as outlined for the preliminary mechanism.

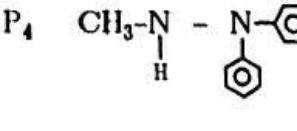
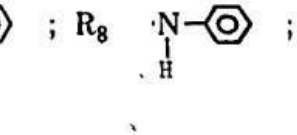
To simplify the procedure the following abbreviations have been made:

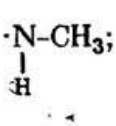
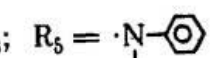
R_1 $\cdot CH_3$; R_1'  ; P CH_4; P'  ;

R_2  ; R_2'  ; R_3 

R_{3A}  ; R_{3B}  ; R_{3C}

P_1  ; P_2  ; P_3

P_4  ; R_8  ; R_4 ; R_6

R_7  ; R_5 =  ; and D 

The rate of nitrogen formation is given by

$$[13] \quad \frac{d[N_2]}{dt} = k_{16}[D] + k_{21}[R_2] + k_{22}[R_2']$$

Referring again to Mulcahy (32) approximations are made that (1) the rate of initiation (R_i) equals the rate of termination (R_t) or

$$[14] \quad \frac{d[R_1]}{dt} = k_{16}[D] - k_{27}[R_2][R_1] - k_{29}[R_2'][R_1] = 0$$

and

$$[15] \quad \frac{d[R_1']}{dt} = k_{16}[D] - k_{28}[R_2][R_1'] - k_{30}[R_2'][R_1'] = 0$$

(2) for long chains, the rate of propagation is given by,

$$[16] \quad \frac{d[R_2]}{dt} = k_{17}[R_1][D] + k_{19}[R_1'][D] - k_{21}[R_2] + k_{31}[R_3][D]$$

$$+ k_{33}[R_{3A}][D] + k_{35}[R_{3B}][D] + k_{37}[R_{3C}][D]$$

$$+ k_{47}[R_4][D] + k_{51}[R_5][D] + k_{45}[R_6][D]$$

$$+ k_{43}[R_7][D] + k_{49}[R_8][D] = 0$$

and

$$[17] \quad \frac{d[R_2']}{dt} = k_{18}[R_1][D] + k_{20}[R_1'][D] - k_{22}[R_2'] + k_{32}[R_3][D]$$

$$+ k_{34}[R_{34}][D] + k_{36}[R_{3B}][D] + k_{38}[R_{3C}][D]$$

$$+ k_{48}[R_4][D] + k_{52}[R_5][D] + k_{46}[R_6][D]$$

$$+ k_{44}[R_7][D] + k_{50}[R_8][D] = 0$$

The other rate equations using the Steady State Approximation are given by:

[18] $$\frac{d[R_4]}{dt} = k_{40}[P_1] - k_{47}[R_4][D] - k_{48}[R_4][D] = 0$$

[19] $$\frac{d[R_5]}{dt} = k_{42}[P_4] - k_{51}[R_5][D] - k_{52}[R_5][D] = 0$$

[20] $$\frac{d[R_6]}{dt} = k_{39}[P_2] + k_{41}[P_3] - k_{45}[R_6][D] - k_{46}[R_6][D] = 0$$

[21] $$\frac{d[R_7]}{dt} = k_{39}[P_2] + k_{42}[P_4] - k_{43}[R_7][D] - k_{44}[R_7][D] = 0$$

[22] $$\frac{d[R_8]}{dt} = k_{40}[P_1] + k_{41}[P_3] - k_{49}[R_8][D] - k_{50}[R_8][D] = 0$$

[23] $$\frac{d[P_1]}{dt} = k_{31}[R_3][D] + k_{32}[R_3][D] - k_{40}[P_1] = 0$$

[24] $$\frac{d[P_2]}{dt} = k_{33}[R_{3A}][D] + k_{34}[R_{3A}][D] - k_{39}[P_2] = 0$$

[25] $$\frac{d[P_3]}{dt} = k_{37}[R_{3B}][D] + k_{38}[R_{3B}][D] - k_{41}[P_3] = 0$$

[26] $$\frac{d[P_4]}{dt} = k_{35}[R_{3C}][D] + k_{36}[R_{3C}][D] - k_{42}[P_4] = 0$$

[27] $$\frac{d[R_3]}{dt} = k_{23}[R_1][D] - k_{31}[R_3][D] - k_{32}[R_3][D] = 0$$

[28] $$\frac{d[R_{3A}]}{dt} = k_{24}[R_1][D] - k_{33}[R_{3A}][D] - k_{34}[R_{3A}][D] = 0$$

$$[29] \quad \frac{d[R_{3B}]}{dt} = k_{25}[R_1'][D] - k_{35}[R_{3B}][D] - k_{36}[R_{3B}][D] = 0$$

$$[30] \quad \frac{d[R_{3C}]}{dt} = k_{26}[R_1'][D] - k_{37}[R_{3C}][D] - k_{38}[R_{3C}][D] = 0$$

By solving for R_3, R_{3A}, R_{3B} and R_{3C} in equations [27] to [30] respectively and then substituting into equations [23] to [26] respectively one obtains:

$$[31] \quad k_{23}[R_1][D] - k_{40}[P_1] = 0$$

$$[32] \quad k_{24}[R_1][D] - k_{39}[P_2] = 0$$

$$[33] \quad k_{25}[R_1'][D] - k_{41}[P_3] = 0$$

$$[34] \quad k_{26}[R_1'][D] - k_{42}[P_4] = 0$$

One next substitutes the expressions for R_3, R_{3A}, R_{3B} and R_{3C} in equations [27] to [30] into equations [16] and [17] to obtain:

$$[35] \quad \frac{d[R_2]}{dt} = k_{17}[R_1][D] + k_{19}'[D] - k_{21}[R_2]$$
$$+ \frac{k_{31}k_{23}[D][R_1]}{k_{31} + k_{32}} + \frac{k_{33}k_{24}[R_1][D]}{k_{33} + k_{34}} + \frac{k_{35}k_{25}[R_1'][D]}{k_{35} + k_{36}}$$
$$+ \frac{k_{37}k_{26}[R_1'][D]}{k_{37}k_{38}} + k_{47}[R_4][D] + k_{51}[R_5][D]$$
$$+ k_{45}[R_6][D] + k_{43}[R_7][D] + k_{49}[R_8][D] = 0$$

and

$$[36] \quad \frac{d[R_2']}{dt} = k_{18}[R_1][D] + k_{20}[R_1'][D] - k_{22}[R_2']$$
$$+ \frac{k_{32}k_{23}[R_1][D]}{k_{31} + k_{32}} + \frac{k_{34}k_{24}[R_1][D]}{k_{33} + k_{34}} + \frac{k_{36}k_{25}[R_1'][D]}{k_{35} + k_{36}}$$

$$+ \frac{k_{38}k_{26}[R_1']}{k_{37} + k_{38}} + k_{48}[R_4][D] + k_{52}[R_5][D]$$

$$+ k_{46}[R_6][D] + k_{44}[R_7][D] + k_{50}[R_8][D] = 0$$

By solving for P_1, P_2, P_3 and P_4 in equations [31] to [34] respectively, and substituting into [18] to [22] one obtains:

$$[37] \quad [R_4] = \frac{k_{23}[R_1]}{k_{47} + k_{48}}$$

$$[38] \quad [R_5] = \frac{k_{26}[R_1']}{k_{51} + k_{52}}$$

$$[39] \quad [R_6] = \frac{k_{24}[R_1] + k_{26}[R_1']}{k_{45} + k_{46}}$$

$$[40] \quad [R_7] = \frac{k_{24}[R_1] + k_{26}[R_1']}{k_{43} + k_{44}}$$

$$[41] \quad [R_8] = \frac{k_{23}[R_1] + k_{25}[R_1']}{k_{49} + k_{50}}$$

By substituting [37] to [41] into [35] and [36] respectively and making the following substitutions:

$$k_x = k_{17} + \frac{k_{31}k_{23}}{k_{31} + k_{32}} + \frac{k_{33}k_{24}}{k_{33} + k_{34}} + \frac{k_{47}k_{23}}{k_{47} + k_{48}}$$

$$+ \frac{k_{45}k_{24}}{k_{45} + k_{46}} + \frac{k_{43}k_{24}}{k_{43} + k_{44}} + \frac{k_{49}k_{23}}{k_{49} + k_{50}}$$

$$k_y = k_{19} + \frac{k_{35}k_{25}}{k_{35} + k_{36}} + \frac{k_{37}k_{26}}{k_{37} + k_{38}} + \frac{k_{51}k_{26}}{k_{51} + k_{52}}$$

$$+ \frac{k_{45}k_{25}}{k_{45} + k_{46}} + \frac{k_{43}k_{26}}{k_{43} + k_{44}} + \frac{k_{49}k_{25}}{k_{49}k_{50}}$$

$$k_z = k_{18} + \frac{k_{32}k_{23}}{k_{31} + k_{32}} + \frac{k_{34}k_{24}}{k_{33} + k_{34}} + \frac{k_{48}k_{23}}{k_{47} + k_{48}}$$

$$+ \frac{k_{46}k_{24}}{k_{45} + k_{46}} + \frac{k_{44}k_{24}}{k_{43} + k_{44}} + \frac{k_{50}k_{23}}{k_{49} + k_{50}}$$

and

$$k_w = k_{20} + \frac{k_{36}k_{25}}{k_{35} + k_{36}} + \frac{k_{38}k_{26}}{k_{37} + k_{38}} + \frac{k_{52}k_{26}}{k_{51} + k_{52}}$$

$$+ \frac{k_{46}k_{25}}{k_{45} + k_{46}} + \frac{k_{44}k_{26}}{k_{43} + k_{44}} + \frac{k_{50}k_{25}}{k_{49} + k_{50}}$$

one obtains:

[42] $$\frac{d[R_2]}{dt} = k_x[R_1][D] + k_y[R_1'][D] - k_{21}[R_2] = 0$$

[43] $$\frac{d[R_2']}{dt} = k_z[R_1][D] + k_w[R_1'][D] - k_{22}[R_2'] = 0$$

By solving for $[R_2]$ and $[R_2']$ in equations [42] and [43], substituting into [14] and [15] and then rearranging one obtains:

[44] $$[D]\frac{k_{27}k_x}{k_{21}}[R_1]^2 + \frac{k_{27}k_y}{k_{21}}[R_1][R_1'] + \frac{k_{29}k_z}{k_{22}}[R_1]^2 + \frac{k_{29}k_w}{k_{22}}[R_1][R_1'] - k_{16} = 0$$

[45] $$[D]\frac{k_{28}k_x}{k_{21}}[R_1][R_1'] + \frac{k_{28}k_y}{k_{21}}[R_1']^2 + \frac{k_{30}k_z}{k_{22}}[R_1][R_1'] + \frac{k_{30}k_w}{k_{22}}[R_1']^2 - k_{16} = 0$$

Dividing through by [D] and letting

$$a = \frac{k_{27}k_x}{k_{21}}; \quad b = \frac{k_{27}k_y}{k_{21}}; \quad c = \frac{k_{29}k_z}{k_{22}}; \quad d = \frac{k_{29}k_w}{k_{22}};$$

$$a' = \frac{k_{28}k_x}{k_{21}}; \quad b' = \frac{k_{28}k_y}{k_{21}}; \quad c' = \frac{k_{30}k_z}{k_{22}}; \quad d' = \frac{k_{30}k_w}{k_{22}};$$

$$x = [R_1]; \quad y = [R_1']; \quad \text{and} \quad e = -k_{16}$$

one obtains:

[46] $ax^2 + bxy + cx^2 + dxy + e = 0$

[47] $a'xy + b'y^2 + c'xy + d'y^2 + e = 0$

rearranging:

[48] $(a+c)x^2 + (b+d)xy + e = 0$

[49] $(b'+d')y^2 + (a'+c')xy + e = 0$

Solving [48] for y, substituting into [49] and then multiplying through by x^2 one obtains:

$$[50] \quad \frac{e^2(b'+d')}{(b+d)^2} - \frac{2e(a+c)(b'+d')}{(b+d)}x^2 + \left[\frac{a+c}{b+d}\right]^2 (b'+d')x^4$$

$$+ \frac{e(a'+c')}{(b+d)}x^2 - (a'+c')(a+c)x^4 + cx^2 = 0$$

and by rearranging and solving for x one obtains:

$$[51] \quad [R_1] = x = \pm \left[\frac{+2e(a+c)(b'+d')}{(b+d)^2} + \frac{-e(a'+c')}{b+d} + e\right] \pm \frac{-e(a'+c')}{(b+d)} + e$$

$$+ \frac{2e(a+c)(b'+d')}{(b+d)^2} - 4\left[\left(\frac{a+c}{b+d}\right)^2 (b'+d') - (a'+c')(a+c)\right]$$

$$\left[\frac{e^2(b'+d')}{(b+d)^2}\right] \Big/ 2\left[\left(\frac{a+c}{b+d}\right)^2 (b'+d') - (a'+c')(a+c)\right]$$

Similarly for y, by solving [49] for x and substituting into [48] one obtains

$$[52] \quad [R_1'] = y = \pm \left[\frac{2e(b'+d')(a+c)}{(a'+c')^2} - \frac{e(b+d)}{(a'+c')} + e\right] \pm \frac{-e(b+d)}{(a'+c')} + e$$

$$+ \frac{2e(b'+d')(a+c)}{(a'+c')^2} - 4\left[\left(\frac{b'+d'}{a'+c'}\right)^2 (a+c) - (b+d)(b'+d')\right]$$

$$\left[\frac{e^2(a+c)}{(a'+c')^2}\right] \Big/ 2\left[\left(\frac{b'+d'}{a'+c'}\right)^2 (a+c) - (b+d)(b'+d')\right]$$

The expressions for $[R_1]$ or x and $[R_1']$ or y are composed of constants; therefore by substituting back into equations [42] and [43] one obtains:

$$[53] \quad [R_2] = \frac{k_x[R_1][D] + k_y[R_1'][D]}{k_{21}} \quad \text{and}$$

$$[54] \quad [R_2'] = \frac{k_z[R_1][D] + k_w[R_1'][D]}{k_{22}}$$

By substituting [53] and [54] into equation [13] one obtains the rate expression for nitrogen formation:

$$[55] \quad \frac{d[N_2]}{dt} = \left[k_{15} + (k_x + k_z)[R_1] + (k_y + k_w)[R_1']\right][D]$$

which is first order for nitrogen formation with respect to the concentration of 1-methyl-2-phenyldiazene because all terms within the square brackets are constants.

5. Comments on the Results with Propene

There seems to be a difference of opinion regarding the usefulness of unsaturated hydrocarbons as chain inhibitors. For example, Forst (5) determined that ethylene and propene had different minimum (or nearly so) rates which were greater than that found with nitric oxide for the pyrolysis of azomethane. Meanwhile others use ethylene (4), cyclohexene (28), propene (6) etc. as inhibitors. Even though the problem is not resolved, it is interesting to speculate on the effect of propene by assuming that, in Run #223, which was the run with the highest ratio of propene to diazene, an elementary rate constant was measured. The value, Figure 12, is 1.64×10^{-5} s^{-1} at 559.05 K. Although we do not yet know the value of the pre-exponential factor in propene, the accepted pre-exponential factor for simple fission of azomethane is in the order or 10^{17}. If this value is substituted in the Arrhenius equa-

tion as a guess† one obtains a value of 233 kJ/mole for the activation energy which is exactly the same as Forst and Rice (5) obtained for the NO inhibited decomposition of azomethane!

Because both azomethane and 1-methyl-2-phenyldiazene have the same activation energy (if the speculation has any validity), one bond fission at the methyl end is indicated. This result lends credence to Engel's hypothesis (3) that the more asymmetrical the functional groups of the diazene the more likely there is to be one bond rather than two-bond fission.

6. Speculation on the Effect of Storage

It was unfortunate that the initial experiments with propene showed no effect of inhibitation of the rate of nitrogen formation, and the wrong conclusions were initially drawn. The reason for this phenomenon remains a mystery. However, it is possible that the effect was due to the conversion of a small amount of the diazene to the *cis* isomer during overnight storage at 105 °C. *Cis* isomers of diazenes are known to be reactive (3,25). Thus the apparent increased rate of nitrogen formation may have been due to pyrolysis of *cis*-1-methyl-2-phenyldiazene which by coincidence compensated for the reduction in rate which was caused by propene.

7. Speculation on the Role of Phenylhydrazone

The presence of aniline, sometimes in quite large yields (see Appendix B), indicates that there is another source in addition to the decomposition of the diazene, as outlined above.

---

† The Arrhenius plots of the uninhibited decomposition of 1-methyl-2-phenyldiazene in both packed and unpacked vessels deserves a comment. Both illustrate excellent fits to the Arrhenius equation but yet, as has been shown, the data were best interpreted by a chain reaction, complicated functions of rate constants. In addition, there may be non-chain contributions to the rate constant. Nevertheless no curvature in the Arrhenius plot is observed even though one might expect it because of the complicated temperature dependence of the rate equation. This seems to show the insensitivity of the Arrhenius equation to such complexities.

It is possible that phenylhydrazone, which was among the reaction products, reacts in the gas phase or on a surface, to give aniline. In solution, during the steps in the synthesis in which phenylhydrazone is converted to diazene, it decomposes partially to aniline and hydrogen cyanide (29). So it seems possible that some of the 1-methyl-2-phenyldiazene isomerizes during pyrolysis, to phenylhydrazone which subsequently decomposes to aniline and hydrogen cyanide.

The difficulty with proposing the above reaction is that no hydrogen cyanide has been found in the reaction products. There may be two reasons. One, it may volatilize when the condensed fraction is warmed to ambient temperature. Another possible explanation may be that it adds across the nitrogen double bond of 1-methyl-2-phenyldiazene, as it has been shown (39) that phenylhydrazones readily add hydrogen cyanide.

Hydrogen cyanide has, however, been detected in the products of decomposition of azomethane (37) using mass spectrometry. However the validity of this report has been questioned on the grounds that only a fragment of some larger molecule was observed. In support of this view the electron impact mass spectrum of azomethane has a peak at m/e of 27 (38) which is only 4% of the parent ion peak, while Wacks work (37) shows that peak at m/e of 27 is prominent in the flow through pyrolysis of azomethane using a mass spectrometer as the mode of detection indicating that an ion of m/e 27 is a product of the pyrolysis of azomethane.

8. Comments on the Erratic Behavior of Rate of Reaction

After the initial set of runs with propene, as described in the results section, a reaction of 1-methyl-2-phenyldiazene with propene was allowed to go to 99% completion. In most subsequent experiments the rate of nitrogen formation was high while the rate of methane formation was low, relative to the rates observed in the previous experiments, (Table 9).

Surface reactions provide a possible explanation of the erratic behavior, if, during the 99% reaction the reaction vessel became coated† (with polypropylene perhaps). Such a surface could provide sites for certain reactions. If reactions [23] to [26] were favored over reactions [17] to [20] an increase in the rate of formation of nitrogen could be observed because the "amine" chain produces three diazene radicals for each one consumed, as opposed to one in the abstraction route. This route would also lower the yield of methane because it consumes a methyl radical. It is interesting to notice the possibility of a branching chain, consistent with erratic behavior and high rate of reaction. Finally it should be noted that the problem of erratic behavior was not solved until a clean reaction vessel was installed.

9. Summary and Suggestions for Future Research

Among the results of this study, four important features related to nitrogen formation emerged. The first is the value of the Arrhenius activation energy, which is less than the value which would be expected of elementary C-N bond rupture at either site. The second feature is the low value of the pre-exponential factor, which is two or three orders of magnitude below the value expected of a simple fission reaction. The inhibiting effect of propene represents the third feature. These observations were interpreted by means of a chain reaction. However, the observation that the order is almost unity, which is the fourth feature, is not in accord with the kind of chain reaction which is usually proposed. A different type of termination reaction was suggested in order to account for the low value of the order.

The length of the chain and the relative contribution of the chain cannot be deduced from the results of this study. Thus, the effect of propene is quite small, leading one to believe that the chains are short. Conversely the values of the

---

† It is interesting and confusing to notice that the packed vessel, in which no propene was used, seemed to develop the same properties.

Arrhenius parameters differ very much from those expected of simple fission reactions; this leads to the suspicion that the chains are quite long. Alternatively, a different pathway,in addition to the chain, may be available, perhaps through isomerization and pyrolysis of cis 1-methyl-2-phenyldiazene.

That the rate of nitrogen formation for the run with the highest ratio of propene to diazene gives the same activation energy (when the value of the pre-exponential factor is guessed) as that for azomethane in the presence of nitrous oxide is interesting. A detailed study, in which the determination of the fully inhibited rate of nitrogen formation would be determined, seems to be warranted. Also, a more detailed study of the various products and the kinetics of their formation should better establish the nature of the chain.

And finally a study should be designed which would establish the roles, if there are any, played by cis-1-methyl-2-phenyldiazene and phenylhydrazone.

References

1. H.C. Ramsperger, J. Am. Chem. Soc., 1929, **51** 2134.
2. M.J. Perona *et al.*, Int. J. Chem. Kinet., 1973, **5**, 495 and A. Péter, G. Acs and P. Huhn, Int. J. Chem. Kinet., 1984, **16**, 767.
3. P.S. Engel, Chem. Rev., 1980, **80**, 99.
4. D. Barton *et al.*, Can. J. Chem. 1983, **61**, 1712.
5. W. Forst and O.K. Rice, Can. J. Chem., 1963, **41**, 562.
6. C. Steel and A.F. Trotman-Dickenson, J. Chem. Soc., 1959, 975.
7. Y. Paquin and W. Forst, Int. J. Chem. Kinet., 1973, **5**, 691.
8. A. Leiba and I. Őref, J. Chem. Soc. Faraday Trans., 1979, **75**, 2694.
9. M. Page *et al.*, J. Chem. Soc., 1953, 3878.
10. G. Chiltz *et al.*, J. Phys. Chem., 1962, **66**, 1426.
11. O.K. Rice and D.V. Sickman, J. Chem. Phys., 1936, **4**, 242.
12. H.A. Taylor and F.D. Jahn, J. Chem. Phys., 1939, **7**, 470.
13. R.M. Marshall and N.D. Page, J. Chem. Soc. Faraday Trans., 1978, **74(8)**, 2121.
14. M.C. Lin and K.J. Laidler, Can J. Chem., 1966, **44**, 2927.
15. S.W. Benson and H.E. O'Neal in Kinetic Data on Gas Phase Unimolecular Reactions, National Bureau of Standards (United States), 1970, p. 31.
16. D.F. McMillen *et al.*, J. Phys. Chem., 1982, **86**, 709.
17. P.L. Holt *et al.*, J. Am. Chem. Soc., 1985, **107**, 2180.
18. N.A. Porter *et al.*, J. Am. Chem. Soc., 1977, **99**, 1264.
19. W.A. Pryor and K. Smith, J. Am. Chem. Soc., 1970, **92**, 5403.
20. R.C. Neuman and G.D. Lockyer, J. Am. Chem. Soc., 1983, **105**, 3982.

21. R.C. Neuman *et al.*, Tetrahedron Lett., 1972, 1221.

22. R.C. Neuman and G.A. Binegar, J. Am. Chem. Soc., 1983, **105**, 135.

23. T. Asano and T. Okaga, J. Org. Chem., 1984, **49**, 4387.

24. S. Seltzer and F.J. Dunne, J. Am. Chem. Soc., 1965, **87**, 2628.

25. N.A. Porter and L.J. Marnett, J. Am. Chem. Soc., 1973, **95**, 4361.

26. K.R. Kopecky *et al.*, Can. J. Chem., 1976, **54**, 2639.

27. J.J. Dannenberg and D. Rocklin, J. Org. Chem., 1982, **47**, 4529.

28. G. Martin and S. Costi, React. Kinet. Catal. Lett., 1981, **17(1)**, 175.

29. B.V. Ioffe and V.S. Stopskii, Dok. Akad. Nauk SSSR, 1966, **175**, 1064.

30. W.E. Wentworth, J. Chem. Educ., 1964, **42(2)**, 96.

31. W.E. Wentworth, J. Chem. Educ., 1964, **42(3)**, 162.

32. M.F.R. Mulcahy in Gas Kinetics, Thomas Nelson and Sons Ltd (Canada), 1983, p. 87.

33. M.T. MacPherson *et al*, Chem. Phys. Lett., 1983, **94**, 430.

34. R.J. Robinson and K.A. Holbrook in Unimolecular Reactions, Wiley, London, 1972, p. 238.

35. N.S. Isaacs in Reaction Intermediates in Organic Chemistry, Wiley, London, 1974, p. 419.

36. S.W. Benson and H.E. O'Neal in Kinetic Data on Gas Phase Unimolecular Reactions, National Bureau of Standards (United States), 1970, p 445.

37. M.E. Wacks, J. Phys. Chem., 1964, **68**, 2725.

38. W. Forst and Z. Prásil, J. Am. Chem. Soc., 1968, **90**, 3344.

39. W. Miller and J. Plöchl, Ber., 1892, **25**, 2057.

40. A. Cornu and R. Massot in Compilation of Mass Spectral Data (2nd ed.), Heyden, London, 1975.

41. O.P. Strausz *et al.*, Can. J. Chem., 1969, **47**, 3470.

42. A.F. Trotman-Dickenson *et al.*, J. Chem. Soc., 1964, 3584.

43. D. Chang and O.K. Rice, Int. J. Chem. Kinet., 1969, **1**, 171.

44. M.A. Koznetsou and A.A. Suvorov, J. Org. Chem. of U.S.S.R., 1982, **18(3)**, 1684.

45. A. Péter, G. Acs and P. Huhn, Int. J. Chem. Kinet., 1984, **16**, 781.

Appendix A

To confirm the identity of the starting material as 1-methyl-2-phenyldiazene a sample of purified material was removed from the line and submitted for a high resolution mass spectrograph, the results of which are listed in Table 10.

The calculated mass of $C_7H_8N_2$ is 120.0687 and what was found was 120.0683. Expected major fragments of the molecule such as $C_6H_5N_2^+$, $C_6H_5N^+$, and $C_6H_5^+$ were found at 105.0450, 92.0499 and 77.0382 respectively. The calculated masses for these fragments are 105.0451, 92.0500 and 77.0391 respectively.

The above results provide evidence that the starting material was 1-methyl-2-phenyldiazene.

AV. MASS	AV. INT. MOD. (%)	STANDARD DEV. (MMU)	DEV. (PPM)	NO. MEASUREMENTS
123.9928	0.40	0.9	7.3	15
121.0720	0.27	0.9	7.7	10
120.0683	5.23	0.7	6.2	19 *
119.9948	0.47	1.0	8.0	18
119.0606	0.82	0.9	7.4	17
116.9953	0.07	1.0	8.4	3
113.0009	2.28	1.0	8.8	19
106.0487	1.40	1.0	9.8	19
105.0450	20.26	0.6	5.4	19
101.0011	0.98	0.5	4.9	19
95.0104	0.54	0.6	6.7	17
93.0561	0.51	1.5	15.9	15
92.0499	3.35	0.8	8.2	18
91.0545	1.26	0.9	9.4	19
91.0419	0.48	1.0	11.3	14
88.0171	0.02	0.0	0.0	1
86.9617	0.09	2.1	24.4	4
84.9648	0.94	0.9	10.2	19
83.0102	0.06	0.2	2.1	3
82.0022	0.26	1.1	13.6	12
79.0449	0.02	0.0	0.0	1
78.0419	3.59	0.7	9.4	19
77.0382	54.54	0.7	8.5	19
76.0304	0.91	0.8	11.0	18
75.0225	0.72	0.8	11.1	18
75.0034	0.06	0.4	5.3	3
74.0150	1.25	0.6	7.5	18
73.0069	0.14	0.5	6.2	5
69.9984	1.27	0.5	6.8	19
66.0454	0.37	1.5	23.2	10
65.0399	4.51	0.5	7.3	19
65.0248	0.56	2.6	40.2	16
64.0321	1.22	0.6	9.7	18
64.0196	0.78	0.6	8.8	18
63.0243	1.94	0.5	8.2	18
63.0113	0.17	0.5	7.3	8
62.0165	0.66	0.8	12.5	17
61.0082	0.39	0.6	9.1	14
52.0242	1.50	2.8	53.8	20
51.0232	20.02	0.2	4.4	19
50.0144	5.33	0.4	8.1	19
49.9953	0.60	0.5	9.9	17
43.0191	5.46	0.9	20.6	19
39.9474	1.83	0.7	17.7	15
39.0083	4.09	0.9	22.2	17
38.0001	2.46	0.9	23.6	15
36.9919	0.11	0.0	0.0	1
31.9741	36.40	1.0	30.6	19
30.9834	0.48	0.7	21.6	4
28.9910	0.11	0.0	0.0	1
28.0093	0.11	0.0	0.0	1
27.9955	100.00	1.1	39.2	19
27.0154	2.15	1.3	47.1	15

□. OF SCANS AVERAGED = 19
V. STD. DEV. (PPM) = 13.9

Table 11. High resolution mass spectra of starting material for kinetic experiments.

Appendix B

To identify the impurity in the starting material and the products found in the condensed fraction, a sample of starting material from the spinning band column and the vacuum line along with the consolidated condensed fraction of three runs were run on a capillary gas chromatograph with a mass spectrometer as the detector.

Gas chromatograph conditions were:

(i) 30 m DB-1 capillary column

(ii) 1 μl injection split 40 to 1

(iii) injector temperature 100 ° C

(iv) Temperature program was 70 ° C for ten minutes then 10 ° C per minute to 230 ° C.

(v) Mass-spectrometry detection was by electron impact.

Figure 17 is the total ion current of the gas chromatograph of the 1-methyl-2-phenyldiazene from the spinning band column. The Y-axis is the percent intensity of the peaks based on saturation of the ion detector of the mass spectrometer. The X-axis has two scales. The lower one is the time scale from injection in minutes and the upper is the scan number.

Other than the 1-methyl-2-phenyldiazene there are peaks at scan numbers 504 and 918 with trace peaks at scan numbers 104 and 207. Tables 12 through 15 are the mass spectra of scan numbers 104, 207, 504 and 918 respectively while Table 16 is a representative mass spectra of 1-methyl-2-phenyldiazene, scan number 200.

The peak at scan number 504 has a mass spectrum which matches that of 1-methyl-2-phenyldiazene. It has been assigned to the *cis* isomer of 1-methyl-2-phenyldiazene.

The peak at scan number 918 also has a molecular ion of 120. Its fragmenta-

tion pattern, however, does not match that of the diazenes but that of phenylhydrazone (44).

From ref 40, the peak at scan number 104 has been identified as benzene while the spectra of the peak of scan number 207 matches that of diethylene glycol, a likely impurity in ethylene glycol.

Fig 18 is the total ion current of the gas chromatograph of the starting material from the vacuum line. As with the chromatograph of the spinning band material there is a peak at scan number 940, Table 17, which matches the mass spectra of scan number 918 of the spinning band material with trace amounts at scan numbers 98, 214 and 510 whose mass spectra are listed in Tables 18 through 20, respectively. The latter three spectra match those of the material from the spinning band column.

Fig 19 is the total ion current of the gas chromatograph of the consolidation of the condensed fraction from three runs. There are peaks at scan numbers 89, 107, 124, 129, 432, 443, 469, 506, 936 and 1515 whose mass spectra are listed in Tables 21 through 30, respectively. There is a trace amount at scan number 212, whose spectra, Table 31, indicates that it is the diethylene glycol impurity. There are also several trace amounts of material at scan numbers greater than phenylhydrazone, scan number 936. The amounts are so small that they could not be identified. The signals could be due to baseline noise.

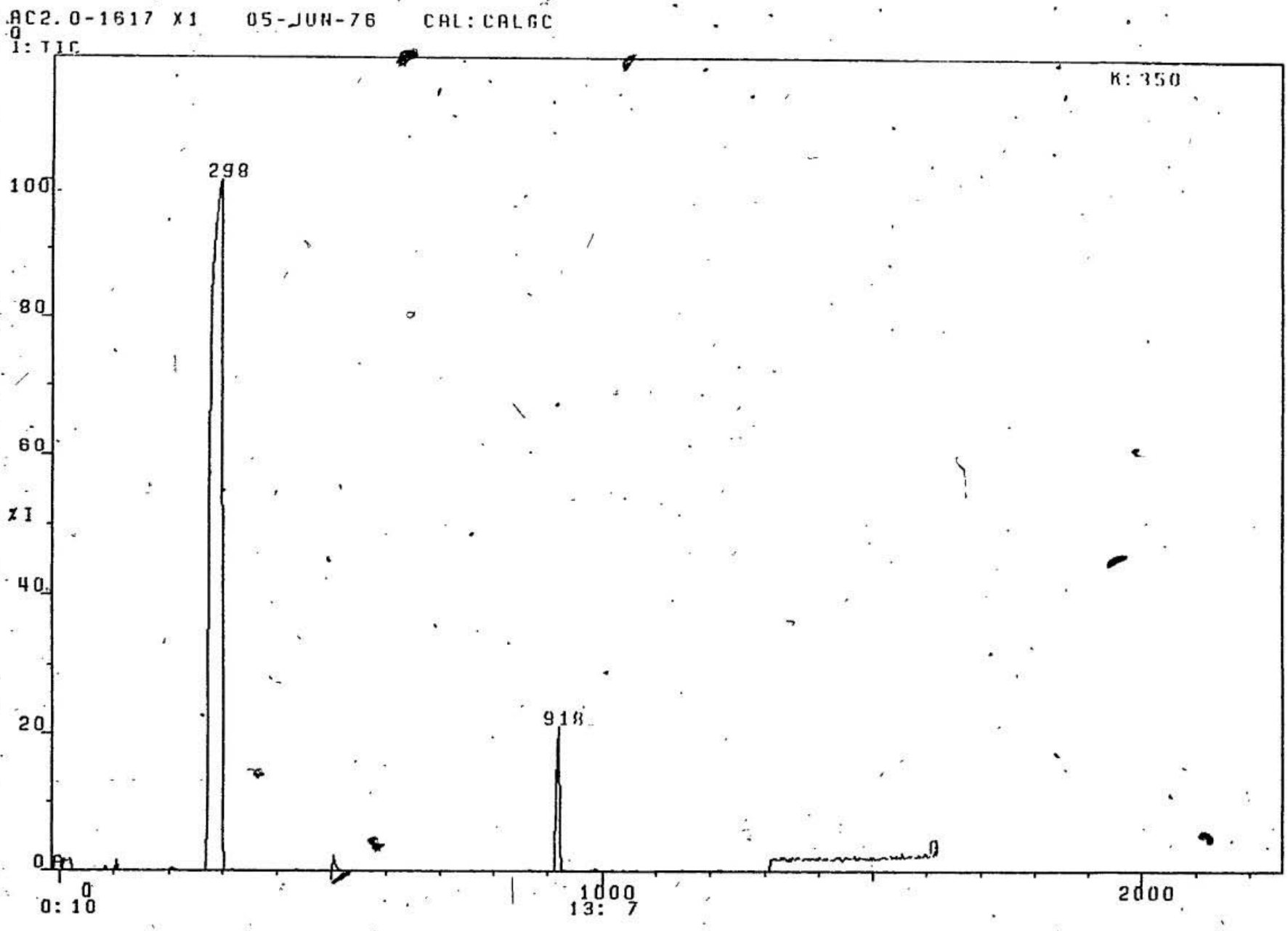
Peaks at scan numbers 89, 107, 506 and 936 were found in small amounts in the starting material and were assigned to formamidine or hydroxylamine, benzene, *cis* 1-methyl-2-phenyldiazene, and phenylhydrazone respectively. From ref 40 the peak at scan number 129 was assigned to toluene; the one of scan number 432 to N-methylaniline; the one at scan number 443 to 1-phenyl-2-ethyldiazene; the one at scan number 469 to 1-benzyl-2-methyldiazene; and the one at scan number 1515 to azobenzene. The spectra of the peak at scan number 124 could not be interpretated and, as with the formamidine or hydroxylamine peak, we have no plausible

explanation for its presence among the products of the reaction. A suspicion is that some of the material on the column was oxidized by air, which is a one percent impurity in the helium carrier gas of the gas chromatograph.

Tables 32 and 33 are mass spectra of scan numbers 275 and 306 which are the 1-methyl-2-phenyldiazene peak as it starts to elute from the column and as it apparently stops eluting. The spectra of scan number 275 matches that of 1-methyl-2-phenyldiazene from the starting material but the spectra of scan number 306 matches that of aniline as confirmed by ref 40. The non-polar capillary column does not completely resolve the diazene and aniline peaks while the analytical column, which is moderately polar, does.

Another point to note is that the non-polar capillary column separates 1-phenyl-2-ethyldiazene and 1-benzyl-2-methyldiazene whereas the packed analytical column apparently does not. From this supposition, the peak eluting after aniline on the analytical column was assigned to N-methylaniline, which is more strongly retained on the moderately polar phase, while the two diazenes were assigned to the same peak.

Figure 17. Total ion current of the effluent from the gas chromatograph of the 1-methyl-2-phenyldiazene from the spinning band column.


AC2.0-1617 X1 05-JUN-76 CAL:CALGC
0
1:TIC
K:350
298
100
80
60
%I
40
20
0
918
0
0:10
1000
13: 7
2000

AC2.104 RT 0: 1:27 05-JUN-84 TIC=104 AUTO-GAIN=1 4. 1
CALGC1 BASE INT.=258 B/G SCAN=30 STATUS:1E
MSN1369 MPDGCMS#1 EI LR DIR

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
38.96	12.02	3.13	6.828	31
44.07	0.39	0.10	0.220	1
49.87	13.57	3.53	7.709	35
50.94	12.79	3.33	7.269	33
52.02	15.12	3.94	8.590	39
77.06	15.12	3.94	8.590	39
78.03	100.00	26.03	56.828	258
79.00	6.59	1.72	3.744	17

C_6H_6
mw 78

Table 12. Mass spectra of scan number 104 of 1-methyl-2-phenyldiazene from spinning band column.

AC2.207 RT 0: 2:47 05-JUN-84 TIC=92 AUTO-GAIN=1 3. 1
CALGC1 BASE INT.=80 B/G SCAN=30 STATUS:1E
MSN1369 MPDGCMS#1 EI LR DIR

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
28.96	33.75	2.70	26.471	27
30.88	145.00	11.60	********	116
44.07	0.00	0.00	0.000	0
45.13	27.50	2.20	21.569	22
60.97	100.00	8.00	78.431	80

$C_4H_{10}O_3$;
mw 106

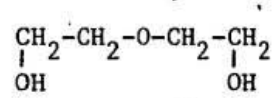


Table 13. Mass spectra of scan number 207 of 1-methyl-2-phenyldiazene from spinning band column.

AC2.504 RT 0: 6:39 05-JUN-84 TIC=95 AUTO-GAIN=1 2. 1.
CALGC1 BASE INT.=216 B/G SCAN=30 STATUS:1E
MSN1369 MPDGCMS#1 EI LR DIR

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
38.03	5.56	1.47	2.353	12
38.96	6.02	1.60	2.549	13
43.07	10.65	2.82	4.510	23
44.07	3.24	0.86	1.373	7
49.87	8.80	2.33	3.725	19
50.94	32.87	8.71	13.922	71
65.11	4.17	1.10	1.765	9
77.04	100.00	26.50	42.353	216
78.01	8.33	2.21	3.529	18
105.02	48.61	12.88	20.588	105
119.95	7.41	1.96	3.137	16

cis $C_7H_8N_2$
mw 120

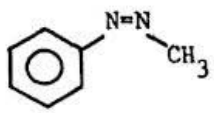


Table 14. Mass spectra of scan number 504 of 1-methyl-2-phenyldiazene from spinning band column.

AC2.918 RT 0:12: 3 05-JUN-84 TIC=422 AUTO-GAIN=1 1. 1
CALGC1 BASE INT.=1342 B/G SCAN=30 STATUS:1E
MSN1369 MPDGCMS#1 EI LR DIR

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
26.28	1.04	1.04	0.240	14
27.21	2.83	2.83	0.650	38
37.09	2.46	2.46	0.565	33
38.03	7.08	7.08	1.626	95
38.96	26.75	26.75	6.145	359
39.85	1.71	1.71	0.394	23
40.93	2.53	2.53	0.582	34
42.01	1.49	1.49	0.342	20
44.07	0.89	0.89	0.205	12
46.60	0.60	0.60	0.137	8
49.87	4.55	4.55	1.044	61
50.94	11.25	11.25	2.585	151
52.01	4.40	4.40	1.010	59
54.09	0.89	0.89	0.205	12
58.98	1.56	1.56	0.359	21
59.45	3.43	3.43	0.787	46
59.91	4.69	4.69	1.078	63
60.95	1.19	1.19	0.274	16
62.00	2.68	2.68	0.616	36
63.05	8.27	8.27	1.900	111
64.08	6.41	6.41	1.472	86
65.10	93.00	93.00	21.363	1248
66.10	8.64	8.64	1.986	116
67.06	0.75	0.75	0.171	10
74.04	1.64	1.64	0.377	22
75.04	0.75	0.75	0.171	10
77.04	7.90	7.90	1.814	106
78.01	1.34	1.34	0.308	18
90.94	6.18	6.18	1.421	83
91.98	100.00	100.00	22.972	1342
93.02	14.83	14.83	3.406	199
105.02	0.97	0.97	0.223	13
117.99	0.89	0.89	0.205	12
118.96	28.02	28.02	6.436	376
119.93	72.73	72.73	16.707	976
120.98	4.77	4.77	1.096	64

$C_7H_8N_2$
mw 120

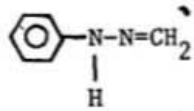


Table 15. Mass spectra of scan number 918 of 1-methyl-2-phenyldiazene from spinning band column.

AC2.299 RT 0: 3.59 05-JUN-84 TIC=1692 AUTO-GAIN=1 1. 1
CALGC1 BASE INT.=4095 B/G SCAN=30 STATUS:1E
MSN1369 MPDGCMS#1 EI LR DIR

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.	MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
25.30	0.29	0.29	0.047	12	121.01	2.64	2.64	0.420	108
26.27	2.08	2.08	0.331	85					
27.21	8.96	8.96	1.427	367					
29.82	0.49	0.49	0.078	20					
30.86	0.24	0.24	0.039	10					
36.11	0.32	0.32	0.051	13					
37.09	7.42	7.42	1.182	304					
37.56	0.63	0.63	0.101	26					
38.03	15.63	15.63	2.489	640					
38.50	2.03	2.03	0.323	83					
38.96	22.27	22.27	3.547	912					
39.85	2.47	2.47	0.393	101					
40.92	3.22	3.22	0.513	132					
42.00	2.91	2.91	0.463	119					
43.07	40.63	40.63	6.471	1664					
44.09	0.00	0.00	0.000	0					
44.60	0.54	0.54	0.086	22					
45.62	1.03	1.03	0.163	42					
46.60	1.15	1.15	0.183	47					
48.95	2.34	2.34	0.373	96					
49.87	37.51	37.51	5.973	1536					
50.93	100.00	100.00	15.925	4095					
52.00	9.18	9.18	1.462	376					
53.06	0.78	0.78	0.124	32					
54.09	0.34	0.34	0.054	14					
58.97	0.22	0.22	0.035	9					
59.88	0.34	0.34	0.054	14					
60.94	3.05	3.05	0.486	125					
62.00	5.45	5.45	0.867	223					
63.05	13.65	13.65	2.174	559					
64.08	12.09	12.09	1.925	495					
65.10	10.72	10.72	1.707	439					
66.10	1.88	1.88	0.299	77					
73.00	1.73	1.73	0.276	71					
74.02	10.31	10.31	1.641	422					
75.04	6.64	6.64	1.058	272					
76.04	7.79	7.79	1.241	319					
77.01	100.00	100.00	15.925	4095					
77.99	32.82	32.82	5.227	1344					
78.96	0.88	0.88	0.140	36					
85.99	0.42	0.42	0.066	17					
86.99	0.66	0.66	0.105	27					
87.96	0.83	0.83	0.132	34					
88.94	0.63	0.63	0.101	26					
89.90	1.17	1.17	0.187	48					
90.97	13.28	13.28	2.116	544					
92.01	3.10	3.10	0.494	127					
93.05	1.27	1.27	0.202	52					
105.04	100.00	100.00	15.925	4095					
106.04	15.60	15.60	2.485	639					
107.04	0.32	0.32	0.051	13					
118.99	0.56	0.56	0.089	23					
119.96	29.47	29.47	4.694	1207					

trans $C_7H_8N_2$
mw 120

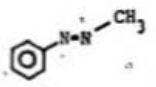
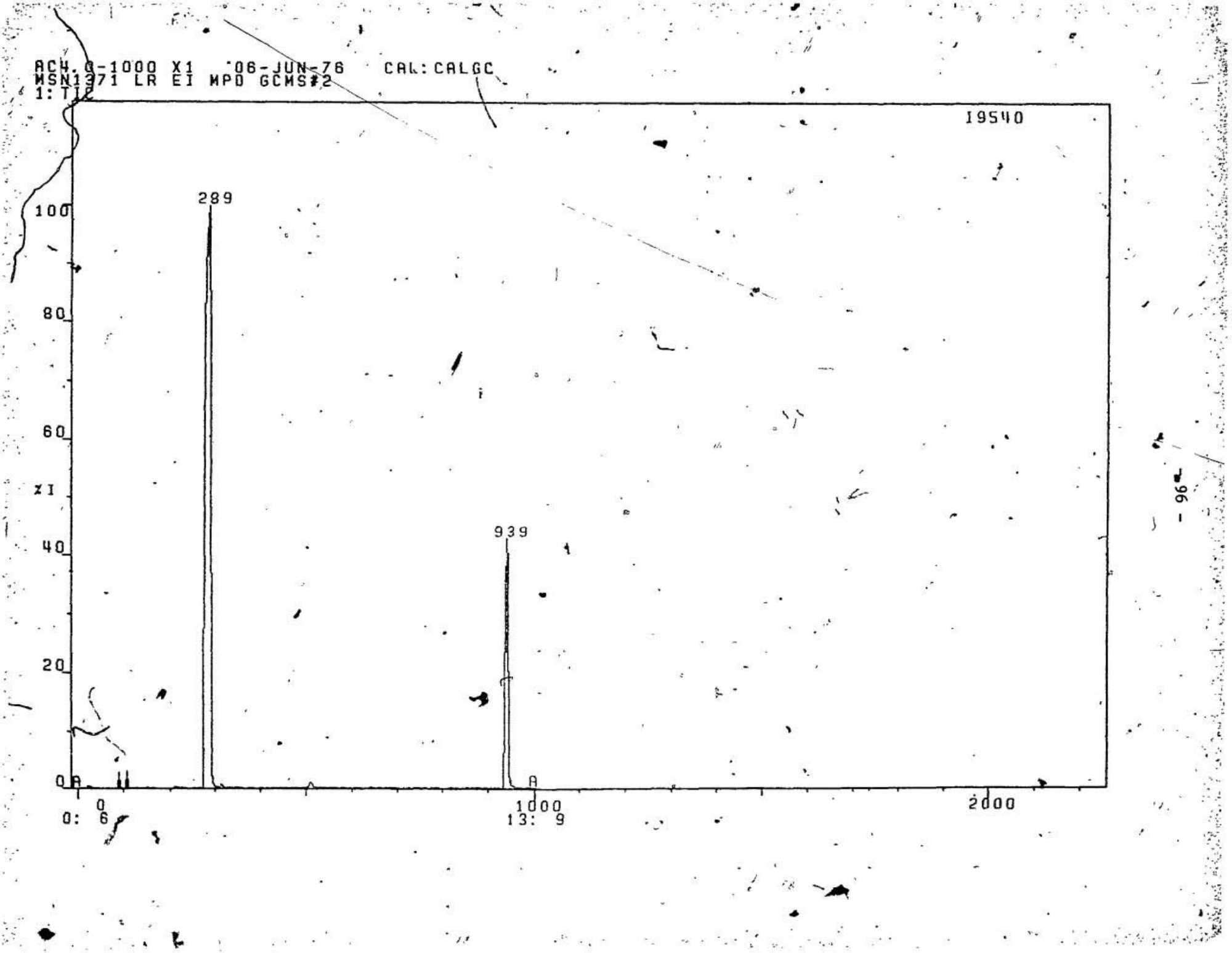


Table 16. Mass spectra of scan number 200 of 1-methyl-2-phenyldiazene from spinning band column.

Figure 18. Total ion current of the effluent from the gas chromatograph of the starting material.


AC4.0-1000 X1 06-JUN-76 CAL:CALGC
MSN1371 LR EI MPD GCMS#2
1:TIC
19540
289
939
100
80
60
40
20
0
XI
A
A
0
0: 6
1000
13: 9
2000

AC4.940 RT 0:12:22 06-JUN-84 TIC=2631 AUTO-GAIN=1 1. 1
CALGC1 BASE INT.=4095 B/G SCAN=30 STATUS:1E
MSN1371 LR EI MPD GCMS#2

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.	MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
26.27	1.90	1.90	0.227	78	77.04	24.98	24.98	2.981	1023
27.21	10.94	10.94	1.305	448	78.01	4.49	4.49	0.536	184
28.09	0.00	0.00	0.000	0	78.96	0.39	0.39	0.047	16
29.82	0.42	0.42	0.050	17	79.92	0.37	0.37	0.044	15
31.96	14.07	14.07	1.678	576	87.00	0.46	0.46	0.055	19
32.54	0.24	0.24	0.029	10	87.98	0.51	0.51	0.061	21
33.61	0.00	0.00	0.000	0	88.95	0.71	0.71	0.085	29
37.09	7.81	7.81	0.932	320	89.90	2.59	2.59	0.309	106
38.03	16.21	16.21	1.935	664	90.99	17.19	17.19	2.051	704
38.96	71.89	71.89	8.579	2944	92.01	100.00	100.00	11.933	4095
39.80	0.46	0.46	0.055	19	93.05	58.22	58.22	6.947	2384
39.85	5.27	5.27	0.629	216	94.07	2.91	2.91	0.347	119
40.94	6.94	6.94	0.828	284	103.05	0.29	0.29	0.035	12
42.02	3.32	3.32	0.396	136	104.06	0.54	0.54	0.064	22
43.07	1.47	1.47	0.175	60	105.06	3.57	3.57	0.425	146
44.07	2.05	2.05	0.245	84	106.06	0.66	0.66	0.079	27
44.61	0.83	0.83	0.099	34	118.85	81.25	81.25	9.695	3327
45.11	0.24	0.24	0.029	10	119.47	0.27	0.27	0.032	11
45.62	2.03	2.03	0.242	83	119.59	0.32	0.32	0.038	13
45.87	0.20	0.20	0.023	8	120.00	100.00	100.00	11.933	4095
45.91	0.22	0.22	0.026	9	121.04	19.51	19.51	2.328	799
45.95	0.49	0.49	0.058	20	122.09	0.71	0.71	0.085	29
46.01	0.24	0.24	0.029	10	138.10	0.27	0.27	0.032	11
46.04	0.29	0.29	0.035	12	157.92	0.29	0.29	0.035	12
46.11	1.05	1.05	0.125	43	183.67	0.42	0.42	0.050	17
46.18	0.32	0.32	0.038	13					
46.61	2.93	2.93	0.350	120					
47.09	0.46	0.46	0.055	19					
48.96	1.32	1.32	0.157	54					
49.87	15.63	15.63	1.865	640					
50.94	36.73	36.73	4.383	1504					
52.01	13.16	13.16	1.571	539					
53.06	1.56	1.56	0.186	64					
54.10	3.49	3.49	0.417	143					
55.12	0.42	0.42	0.050	17					
58.98	4.27	4.27	0.510	175					
59.45	7.01	7.01	0.836	287					
59.91	12.50	12.50	1.492	512					
60.44	1.29	1.29	0.154	53					
60.95	3.49	3.49	0.417	143					
62.01	7.01	7.01	0.836	287					
63.06	21.88	21.88	2.611	896					
64.09	19.90	19.90	2.375	815					
65.10	100.00	100.00	11.933	4095					
66.10	31.26	31.26	3.730	1280					
67.06	2.22	2.22	0.265	91					
68.04	0.39	0.39	0.047	16					
68.93	0.37	0.37	0.044	15					
72.18	0.22	0.22	0.026	9					
73.01	0.54	0.54	0.064	22					
74.04	3.10	3.10	0.370	127					
75.04	2.44	2.44	0.291	100					
76.06	1.95	1.95	0.233	80					

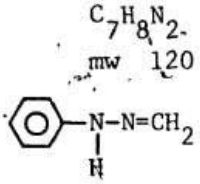


Table 17. Mass spectra of scan number 940 of starting material.

AC4.98 RT 0: 1:22 06-JUN-84 TIC=453 AUTO-GAIN=1
CALGC1 BASE INT.=31 B/G SCAN=30 STATUS:1E
MSN1371 LR EI MPD GCMS#2

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
28.09	0.00	0.00	0.000	0
28.95	74.19	0.56	29.114	23
31.96	********	15.60	********	639
39.80	87.10	0.66	34.177	27
44.07	29.03	0.22	11.392	9
68.95	100.00	0.76	39.241	31
91.00	38.71	0.29	15.190	12

C_6H_6
mw 78

Table 18. Mass spectra of scan number 98 of starting material.

AC4.214 RT 0: 2:52 06-JUN-84 TIC=498 AUTO-GAIN=1 3. 1
CALGC1 BASE INT.=143 B/G SCAN=30 STATUS:1E
MSN1371 LR EI MPD GCMS#2

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
27.21	11.89	0.42	7.456	17
28.09	0.00	0.00	0.000	0
28.96	37.76	1.32	23.684	54
29.80	13.99	0.49	8.772	20
30.88	156.64	5.47	98.246	224
31.96	626.57	21.88	*******	896
34.10	0.00	0.00	0.000	0
39.80	31.47	1.10	19.737	45
45.13	18.18	0.63	11.404	26
60.97	100.00	3.49	62.719	143
68.96	9.09	0.32	5.702	13

$C_4H_{10}O_3$
mw 106

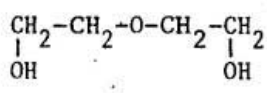


Table 19. Mass spectra of scan number 214 of starting material.

AC4.510 RT 0: 8:46 06-JUN-84 TIC=518 AUTO-GAIN=1 3. 1
CALGC1 BASE INT.=343 B/G SCAN=30 STATUS:1E
MSN1371 LR EI MPD GCMS#2

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
22.14	4.37	0.37	1.736	15
27.21	7.87	0.66	3.125	27
27.22	2.62	0.22	1.042	9
28.09	0.00	0.00	0.000	0
28.96	1.17	0.10	0.463	4
31.96	242.57	20.32	96.296	832
34.10	0.58	0.05	0.231	2
38.04	2.92	0.24	1.157	10
38.96	5.54	0.46	2.199	19
39.80	13.41	1.12	5.324	46
43.07	11.37	0.95	4.514	39
44.07	13.12	1.10	5.208	45
49.88	6.12	0.51	2.431	21
50.94	27.99	2.34	11.111	96
63.06	5.54	0.46	2.199	19
64.08	6.12	0.51	2.431	21
65.11	6.41	0.54	2.546	22
77.04	100.00	8.38	39.699	343
78.01	4.37	0.37	1.736	15
105.02	39.94	3.35	15.856	137
119.95	8.45	0.71	3.356	29

<u>cis</u>-$C_7H_8N_2$
mw 120

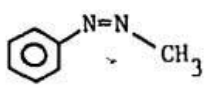
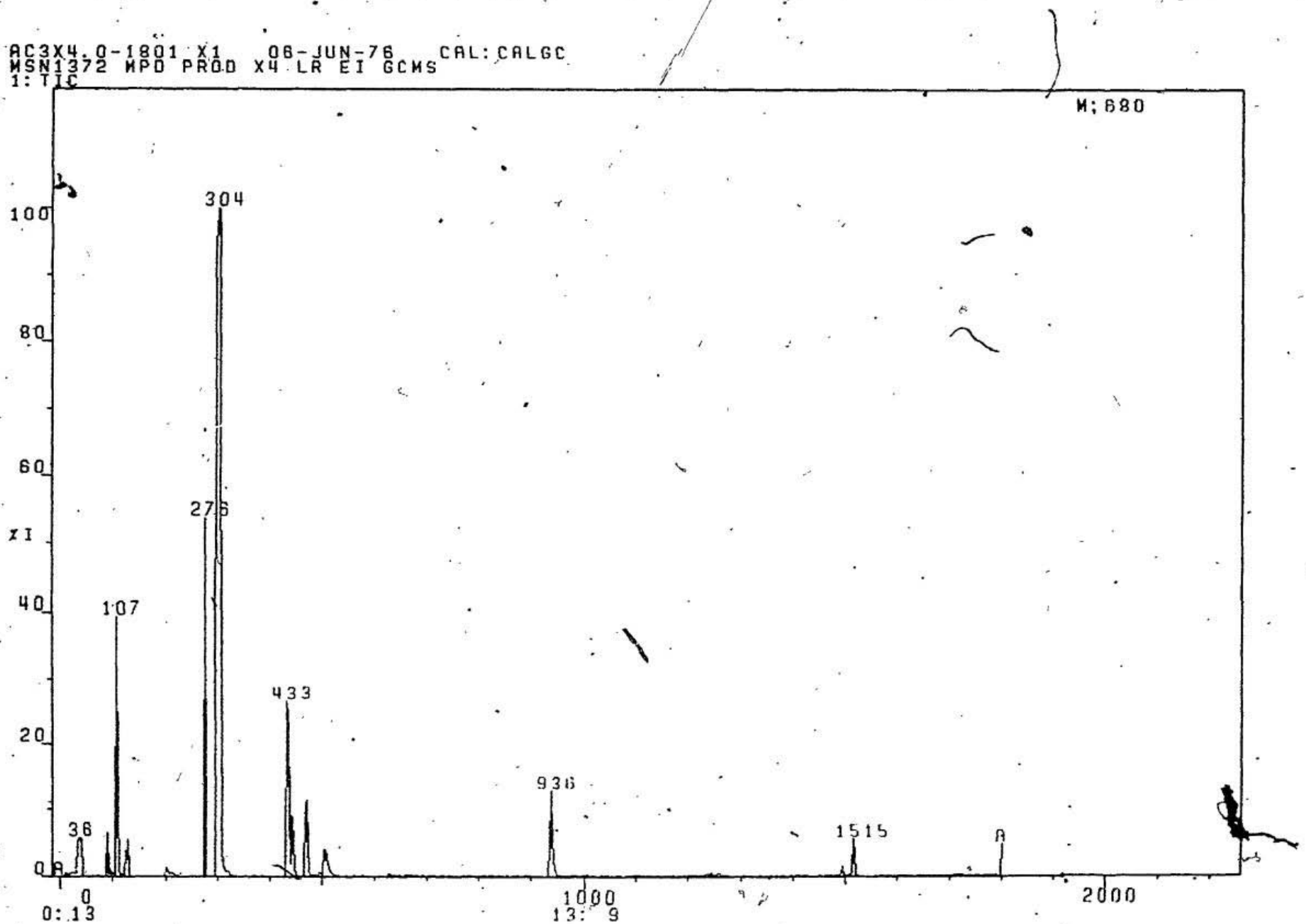


Table 20. Mass spectra of scan number 510 of starting material.

Figure 19. Total ion current of the effluent from the gas chromatograph of the consolidated condensed fraction.


AC3X4.0-1801 X1 06-JUN-76 CAL:CALGC
MSN1372 MPD PROD X4 LR EI GCMS
1:TIC
M;680
304
276
107
433
936
1515
36
100
80
60
40
20
0
XI
0
1000
2000
0:13
13: 9

AC3X4.89 RT 0: 1:15 06-JUN-84 TIC=1105 AUTO-GAIN=1 1. 1
CALGC1 BASE INT.=4042 B/G SCAN=40 STATUS:1E
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
22.16	0.94	0.93	0.596	38
26.29	0.59	0.59	0.376	24
27.21	1.90	1.88	1.207	77
28.09	6.33	6.25	4.013	256
28.97	65.66	64.81	41.605	2654
29.81	0.92	0.90	0.580	37
31.97	69.67	68.77	44.145	2816
33.07	1.21	1.20	0.768	49
34.12	9.08	8.96	5.753	367
36.11	0.79	0.78	0.502	32
39.81	100.00	98.71	63.364	4042
44.10	46.04	45.45	29.174	1861
45.11	0.67	0.66	0.423	27

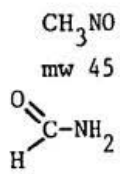


Table 21. Mass spectra of scan number 89 of condensed fraction.

AC3X4.107 RT 0: 1:29 06-JUN-84 TIC=2827 AUTO-GAIN=1 3. 1
CALGC1 BASE INT.=4095 B/G SCAN=106 STATUS: 1E
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
22.14	0.22	0.22	0.024	9
24.29	0.32	0.32	0.035	13
25.31	2.32	2.32	0.256	95
26.28	25.01	25.01	2.762	1024
27.21	24.52	24.52	2.708	1004
28.09	0.00	0.00	0.000	0
29.82	0.22	0.22	0.024	9
34.82	0.22	0.22	0.024	9
34.95	0.34	0.34	0.038	14
36.11	2.86	2.86	0.316	117
36.61	0.32	0.32	0.035	13
37.09	30.48	30.48	3.366	1248
37.57	9.94	9.94	1.098	407
38.03	49.50	49.50	5.466	2027
38.50	2.54	2.54	0.280	104
38.96	100.00	100.00	11.043	4095
39.41	2.32	2.32	0.256	95
39.80	0.20	0.20	0.022	8
39.85	3.17	3.17	0.351	130
40.94	0.32	0.32	0.035	13
45.16	0.32	0.32	0.035	13
48.01	1.76	1.76	0.194	72
48.96	17.97	17.97	1.985	736
49.00	0.29	0.29	0.032	12
49.87	100.00	100.00	11.043	4095
50.94	100.00	100.00	11.043	4095
52.01	99.80	99.80	11.022	4087
53.07	7.79	7.79	0.860	319
59.89	1.25	1.25	0.138	51
60.95	3.71	3.71	0.410	152
62.01	4.22	4.22	0.467	173
63.06	21.86	21.86	2.414	895
64.09	1.83	1.83	0.202	75
71.99	1.07	1.07	0.119	44
73.04	10.55	10.55	1.165	432
74.06	32.41	32.41	3.579	1327
74.19	0.49	0.49	0.054	20
75.09	12.50	12.50	1.381	512
76.08	29.28	29.28	3.233	1199
76.35	3.88	3.88	0.429	159
77.06	100.00	100.00	11.043	4095
77.20	0.42	0.42	0.046	17
77.38	0.39	0.39	0.043	16
78.02	99.49	99.49	10.987	4074
78.11	0.24	0.24	0.027	10
78.98	49.99	49.99	5.520	2047
79.92	1.49	1.49	0.165	61
206.98	0.22	0.22	0.024	9

C_6H_6
mw 78

Table 22. Mass spectra of scan number 107 of condensed fraction.

AC3X4.124 RT 0: 1:42 06-JUN-84 TIC=618 AUTO-GAIN=1 3. 1
CALGC1 BASE INT.=1151 B/G SCAN=123 STATUS:1E
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
22.14	1.48	0.42	0.445	17
26.27	2.00	0.56	0.602	23
27.21	5.39	1.51	1.622	62
28.09	0.00	0.00	0.000	0
29.82	5.47	1.54	1.648	63
31.96	11.03	3.10	3.322	127
38.02	2.17	0.61	0.654	25
38.94	3.39	0.95	1.020	39
39.85	2.78	0.78	0.837	32
40.93	9.64	2.71	2.903	111
42.02	65.77	18.49	19.801	757
43.09	18.07	5.08	5.441	208
44.13	2.35	0.66	0.706	27
45.15	1.30	0.37	0.392	15
52.01	1.65	0.46	0.497	19
56.13	1.91	0.54	0.575	22
57.10	3.56	1.00	1.072	41
58.07	49.96	14.04	15.041	575
59.02	2.43	0.68	0.732	28
66.08	1.13	0.32	0.340	13
67.07	2.52	0.71	0.759	29
68.04	1.56	0.44	0.471	18
69.00	2.69	0.76	0.811	31
73.08	0.70	0.20	0.209	8
83.08	100.00	28.11	30.107	1151
84.10	55.52	15.60	16.715	639
85.10	2.78	0.78	0.837	32

Table 23. Mass spectra of scan number 124 of condensed fraction.

AC3X4.129 RT 0: 1:46 06-JUN-84 TIC=841 AUTO-GAIN=1 1. 1
CALGC1 BASE INT.=2214 B/G SCAN=128 STATUS: 1E
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
26.27	0.59	0.32	0.243	13
28.09	0.00	0.00	0.000	0
31.96	10.12	5.47	4.192	224
37.09	1.76	0.95	0.730	39
38.03	1.04	0.56	0.430	23
38.96	8.45	4.57	3.499	187
40.94	0.81	0.44	0.337	18
45.12	2.48	1.34	1.029	55
45.62	0.77	0.42	0.318	17
46.13	2.62	1.42	1.085	58
49.88	3.25	1.76	1.347	72
50.94	6.05	3.27	2.507	134
52.02	1.17	0.63	0.487	26
53.07	1.08	0.59	0.449	24
60.95	1.76	0.95	0.730	39
62.01	2.17	1.17	0.898	48
63.06	6.46	3.49	2.676	143
64.10	2.03	1.10	0.842	45
65.08	10.93	5.91	4.528	242
66.08	1.90	1.03	0.786	42
67.05	0.41	0.22	0.168	9
68.02	0.00	0.00	0.000	0
73.01	0.59	0.32	0.243	13
74.05	0.72	0.39	0.299	16
77.04	1.40	0.76	0.580	31
86.02	0.68	0.37	0.281	15
87.02	0.54	0.29	0.225	12
88.97	4.70	2.54	1.946	104
89.91	2.53	1.37	1.048	56
90.04	0.86	0.46	0.356	19
90.09	0.72	0.39	0.299	16
90.16	0.54	0.29	0.225	12
90.26	0.77	0.42	0.318	17
90.49	0.54	0.29	0.225	12
90.96	100.00	54.07	41.430	2214
92.02	65.00	35.14	26.927	1439
93.06	5.96	3.22	2.470	132

C_7H_8
mw 92

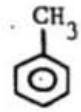


Table 24. Mass spectra of scan number 129 of condensed fraction.

AC3X4.432 RT 0: 5:45 06-JUN-84 TIC=1370 AUTO-GAIN=1 3. 1
CALGC1 BASE INT.=4095 B/G SCAN=431 STATUS=
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
25.30	0.44	0.44	0.114	18
26.28	1.17	1.17	0.304	48
27.21	2.59	2.59	0.671	106
28.09	0.00	0.00	0.000	0
29.82	6.35	6.35	1.646	260
37.09	1.49	1.49	0.386	61
38.03	4.30	4.30	1.114	176
38.49	0.27	0.27	0.070	11
38.96	14.04	14.04	3.639	575
39.80	0.10	0.10	0.025	4
40.93	1.86	1.86	0.481	76
42.02	1.37	1.37	0.354	56
44.07	0.29	0.29	0.076	12
45.62	0.83	0.83	0.215	34
48.95	0.39	0.39	0.101	16
49.87	7.79	7.79	2.019	319
50.94	18.41	18.41	4.772	754
51.48	0.27	0.27	0.070	11
52.01	8.06	8.06	2.089	330
52.54	4.69	4.69	1.215	192
53.06	10.92	10.92	2.829	447
53.58	8.50	8.50	2.203	348
54.10	1.66	1.66	0.430	68
58.75	0.24	0.24	0.063	10
60.94	0.59	0.59	0.152	24
62.00	1.34	1.34	0.348	55
63.05	4.27	4.27	1.108	175
64.08	2.86	2.86	0.741	117
65.10	10.09	10.09	2.614	413
66.10	2.34	2.34	0.608	96
67.05	0.76	0.76	0.196	31
73.00	0.68	0.68	0.177	28
74.04	2.32	2.32	0.601	95
75.04	1.66	1.66	0.430	68
76.04	1.66	1.66	0.430	68
77.02	38.36	38.36	9.944	1571
78.01	11.82	11.82	3.063	484
78.96	15.14	15.14	3.924	620
79.92	1.25	1.25	0.323	51
80.98	0.24	0.24	0.063	10
89.90	0.78	0.78	0.203	32
90.97	0.78	0.78	0.203	32
92.01	3.05	3.05	0.791	125
93.05	0.07	0.07	0.019	3
104.05	6.25	6.25	1.620	256
105.06	4.69	4.69	1.215	192
105.71	0.22	0.22	0.057	9
106.06	100.00	100.00	25.919	4095
107.06	81.27	81.27	21.065	3328
108.04	7.42	7.42	1.924	304
109.02	0.37	0.37	0.095	15

C_7H_9N
mw 106

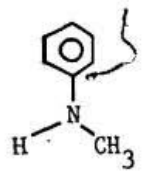


Table 25. Mass spectra of scan number 432 of condensed fraction.

AC3X4.443 RT 0: 5:54 06-JUN-84 TIC=942 AUTO-GAIN=1 1: 1
CALGC1 BASE INT.=3951 B/G SCAN=440 STATUS: 1E
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
22.14	0.13	0.12	0.064	5
26.27	1.01	0.98	0.510	40
27.21	5.37	5.18	2.704	212
28.09	0.00	0.00	0.000	0
28.96	0.53	0.51	0.268	21
28.98	4.99	4.81	2.513	197
29.82	0.38	0.37	0.191	15
37.09	0.99	0.95	0.497	39
38.03	2.15	2.08	1.084	85
38.96	1.92	1.86	0.969	76
40.93	1.04	1.00	0.523	41
42.02	0.66	0.63	0.332	26
44.07	0.53	0.51	0.268	21
48.95	0.58	0.56	0.293	23
49.87	2.78	2.69	1.403	110
50.94	16.50	15.92	8.316	652
52.01	1.44	1.39	0.727	57
55.13	0.38	0.37	0.191	15
62.00	0.86	0.83	0.434	34
63.05	1.82	1.76	0.918	72
64.08	2.51	2.42	1.263	99
65.10	1.37	1.32	0.689	54
74.05	0.86	0.83	0.434	34
75.06	0.89	0.85	0.446	35
76.07	0.76	0.73	0.383	30
77.05	100.00	96.48	50.395	3951
78.02	7.59	7.33	3.827	300
78.99	0.15	0.15	0.077	6
88.98	0.33	0.32	0.166	13
90.97	2.91	2.81	1.467	115
92.01	1.37	1.32	0.689	54
93.05	0.66	0.63	0.332	26
105.04	43.51	41.98	21.926	1719
119.01	0.33	0.32	0.166	13
119.94	0.23	0.22	0.115	9
134.04	3.11	3.00	1.569	123

$C_8H_{10}N_2$
mw 134

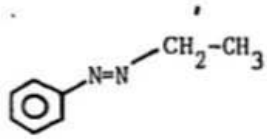
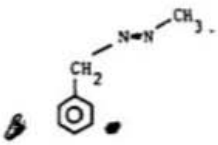


Table 26. Mass spectra of scan number 443 of condensed fraction.

AC3X4 469 RT 0 6.14 06-JUN-84 TIC=1057 AUTO-GAIN=1 2. 1
CALGC1 BASE INT =4095 B/G SCAN=466 STATUS 1E
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT. MOD	%HT. BASE	% TIC	ABS HT.
22.14	0.34	0.34	0.121	14
26.27	0.39	0.39	0.150	16
27.21	2.20	2.20	0.843	90
28.09	0.00	0.00	0.000	0
29.82	0.46	0.46	0.178	19
31.96	6.25	6.25	2.399	256
37.09	0.29	0.29	0.112	12
38.03	1.88	1.88	0.722	77
38.96	15.16	15.16	5.820	621
40.94	3.17	3.17	1.218	130
42.02	0.49	0.49	0.187	20
43.07	7.03	7.03	2.699	288
45.63	0.68	0.68	0.262	28
46.34	0.20	0.20	0.075	8
48.96	0.49	0.49	0.187	20
49.88	3.61	3.61	1.387	148
50.94	7.23	7.23	2.774	296
52.02	3.05	3.05	1.171	125
53.08	0.54	0.54	0.206	22
60.95	0.76	0.76	0.291	31
62.02	1.56	1.56	0.600	64
63.06	5.86	5.86	2.249	240
64.09	2.81	2.81	1.078	115
65.11	37.24	37.24	14.291	1525
66.08	2.08	2.08	0.797	85
68.93	0.42	0.42	0.159	17
74.04	1.03	1.03	0.394	42
75.04	0.68	0.68	0.262	28
76.05	0.71	0.71	0.272	29
77.04	3.20	3.20	1.228	131
78.01	1.61	1.61	0.618	66
78.96	0.29	0.29	0.112	12
87.01	0.29	0.29	0.112	12
88.95	3.83	3.83	1.471	157
89.91	1.27	1.27	0.487	52
90.96	100.00	100.00	38.375	4095
92.00	6.62	6.62	2.540	271
93.04	0.63	0.63	0.244	26
103.02	0.29	0.29	0.112	12
104.04	1.17	1.17	0.450	48
105.06	0.27	0.27	0.103	11
117.99	0.32	0.32	0.122	13
118.98	34.36	34.36	13.185	1407
119.95	2.66	2.66	1.021	109
130.96	0.22	0.22	0.084	9
132.00	0.22	0.22	0.084	9
134.04	5.76	5.76	2.212	236
135.05	0.46	0.46	0.178	19

$C_8H_{10}N_2$
mw 134



or

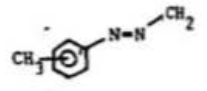


Table 27. Mass spectra of scan number 469 of condensed fraction.

AC3X4.506 RT 0: 6:43 06-JUN-84 TIC=589 AUTO-GAIN=1 4. 1
CALGC1 BASE INT.=1511 B/G SCAN=503 STATUS:1E
MSN1372 MPD PROD X4 LR, EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
22.14	1.13	0.42	0.463	17
26.27	0.66	0.24	0.272	10
27.31	2.38	0.88	0.980	36
28.09	0.00	0.00	0.000	0
31.96	2.12	0.78	0.871	32
37.09	1.32	0.49	0.545	20
37.56	0.99	0.37	0.408	15
38.03	3.44	1.27	1.416	52
38.96	4.50	1.66	1.852	68
42.02	0.60	0.22	0.245	9
43.07	9.53	3.52	3.922	144
49.87	9.99	3.69	4.112	151
50.94	29.52	10.89	12.146	446
52.01	2.78	1.03	1.144	42
60.95	0.79	0.29	0.327	12
62.00	0.79	0.29	0.327	12
63.05	3.38	1.25	1.389	51
64.08	2.85	1.05	1.171	43
65.10	2.58	0.95	1.062	39
66.09	0.60	0.22	0.245	9
68.95	1.19	0.44	0.490	18
74.06	2.18	0.81	0.899	33
75.06	2.85	1.05	1.171	43
76.07	2.05	0.76	0.844	31
77.05	100.00	36.90	41.149	1511
78.03	4.90	1.81	2.015	74
88.02	0.79	0.29	0.327	12
90.97	2.25	0.83	0.926	34
92.01	2.12	0.78	0.871	32
93.05	3.11	1.15	1.280	47
105.04	37.00	13.65	15.223	559
106.04	4.04	1.49	1.661	61
119.96	5.82	2.15	2.397	88
206.94	0.86	0.32	0.354	13

$C_7H_8N_2$
mw 120

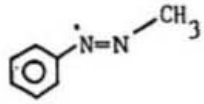


Table 28. Mass spectra of scan number 506 of condensed fraction.

AC3X4.936 RT 0:12:19 06-JUN-84 TIC=1120 AUTO-GAIN=1 3 1
CALGC1 BASE INT.=2687 B/G SCAN=930 STATUS=15
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT MOD	%HT BASE	% TIC	ABS HT	MASS	%HT MOD.	%HT BASE	% TIC	ABS HT
26 27	0 78	0 51	0 174	21	130 87	0 45	0 29	0 100	12
27 21	5 77	3 79	1 298	155					
28 09	0 00	0 00	0 000	0					
37 09	1 90	1.25	0 423	51					
38 03	7 11	4.66	1 585	191					
38.96	23.78	15.60	5.302	639					
39.80	0.86	0 56	0.191	23					
39 85	0.11	0 07	0.025	3					
40 93	2.64	1.73	0.589	71					
42.01	1.79	1.17	0.398	48					
43.07	0.52	0.34	0.116	14					
44.07	0.30	0.20	0.066	8					
44.60	0.45	0.29	0.100	12					
45.61	0.67	0.44	0.149	18					
46.61	1.08	0.71	0.241	29					
48.95	0.41	0.27	0.091	11					
49.87	4.73	3.10	1.054	127					
50.94	13.99	9.18	3.120	376					
52.01	4.28	2.81	0.954	115					
53.07	0.74	0.49	0.166	20					
54.10	0.82	0.54	0.183	22					
58.98	1.94	1.27	0.431	52					
59.44	3.31	2.17	0.738	89					
59.91	2.94	1.93	0.655	79					
60.94	1.08	0.71	0.241	29					
62.01	2.90	1.90	0.647	78					
63.05	9.97	6.54	2.224	268					
64.08	7.70	5.05	1.717	207					
65.10	89.62	58.80	19.978	2408					
66.10	11.87	7.79	2.647	319					
67.06	0.93	0.61	0.207	25					
68.92	0.37	0.24	0.083	10					
74.02	1.38	0.90	0.307	37					
75.04	1.19	0.78	0.265	32					
76.04	1.53	1.00	0.340	41					
77.02	10.16	6.67	2.265	273					
78.01	2.87	1.88	0.639	77					
88.94	0.82	0.54	0.183	22					
89.90	0.41	0.27	0.091	11					
90.94	5.92	3.88	1.319	159					
91.98	100.00	65.62	22.293	2687					
93.02	16.86	11.06	3.758	453					
94.04	0.74	0.49	0.166	20					
105.02	1.56	1.03	0.348	42					
106.02	0.67	0.44	0.149	18					
117.87	0.52	0.34	0.116	14					
118.01	1.56	1.03	0.348	42					
118.46	0.48	0.32	0.108	13					
118.58	0.33	0 22	0.075	9					
118.96	27.35	17.95	6.098	735					
119.93	69.74	45.76	15.548	1874					
120.98	4.84	3.17	1.079	130					
122 01	0 37	0.24	0 083	10					

$C_7H_8N_2$
mw 120

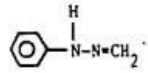


Table 29. Mass spectra of scan number 936 of condensed fraction.

AC3X4.1515 RT 0:19:51 06-JUN-84 TIC=694 AUTO-GAIN=1 3. 1
CALGC1 BASE INT.=2542 B/G SCAN=1511 STATUS: 1E
MSN1372 MPD PROD X4 LF EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
26.28	0.51	0.32	0.241	13
27.22	2.20	1.39	1.037	56
28.09	2.52	1.59	1.185	64
34.10	0.94	0.60	0.444	24
37.09	0.51	0.32	0.241	13
38.03	1.49	0.94	0.704	38
38.96	2.16	1.36	1.018	55
40.93	1.02	0.64	0.481	26
44.07	0.28	0.17	0.130	7
49.87	2.95	1.86	1.389	75
50.94	20.30	12.80	9.554	516
52.01	1.02	0.64	0.481	26
62.01	0.35	0.22	0.167	9
63.05	1.42	0.89	0.667	36
64.09	1.42	0.89	0.667	36
65.11	1.57	0.99	0.741	40
66.08	1.14	0.72	0.537	29
74.04	0.55	0.35	0.259	14
75.06	0.47	0.30	0.222	12
76.04	2.01	1.26	0.944	51
77.04	100.00	63.05	47.065	2542
78.01	6.02	3.79	2.833	153
81.88	0.39	0.25	0.185	10
83.53	0.98	0.62	0.463	25
90.94	0.75	0.47	0.352	19
93.02	1.49	0.94	0.704	38
105.02	21.36	13.47	10.054	543
106.02	1.85	1.17	0.870	47
115.02	0.83	0.52	0.389	21
127.98	0.63	0.40	0.296	16
138.96	0.75	0.47	0.352	19
149.87	0.43	0.27	0.204	11
150.92	1.02	0.64	0.481	26
151.95	5.90	3.72	2.777	150
152.98	4.80	3.03	2.259	122
154.01	1.10	0.69	0.518	28
166.98	1.22	0.77	0.574	31
181.97	20.14	12.70	9.480	512
182.96	2.48	1.56	1.166	63
206.91	0.51	0.32	0.241	13

$C_{12}H_{10}N_2$
mw 182

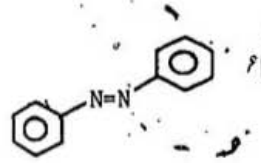


Table 30. Mass spectra of scan number 1515 of condensed fraction.

AC3X4.212 RT 0: 2:51 06-JUN-84 TIC=471 AUTO-GAIN=1 3. 1
CALGC1 BASE INT.=440 B/G SCAN=209 STATUS: 1E
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
27.20	1.36	0.15	1.070	6
28.09	0.00	0.00	0.000	0
28.95	19.32	2.08	15.152	85
29.80	17.95	1.93	14.082	79
30.87	154.09	16.56********		678
39.80	2.95	0.32	2.317	13
44.07	4.55	0.49	3.565	20
52.02	2.95	0.32	2.317	13
59.89	2.50	0.27	1.961	11
60.96	100.00	10.74	78.431	440
62.02	4.55	0.49	3.565	20
74.07	0.45	0.05	0.357	2
78.03	3.64	0.39	2.852	16
88.96	2.27	0.24	1.783	10
90.97	2.73	0.29	2.139	12

$C_4H_{10}O_3$
mw 106

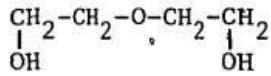


Table 31. Mass spectra of scan number 212 of condensed fraction.

AC3X4 275 RT 0: 3 40 06-JUN-84 TIC=2337 AUTO-GAIN=1 1 1
CALGC1 BASE INT.=4095 B/G SCAN=274 STATUS: 1E
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.	MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
22.14	0.39	0.39	0.052	16	91.84	0.32	0.32	0.043	13
25.31	0.71	0.71	0.095	29	92.03	3.91	3.91	0.524	160
26.27	8.35	3.35	0.449	137	93.05	1.66	1.66	0.223	68
27.21	22.95	22.95	3.078	940	103.05	0.34	0.34	0.046	14
28.09	0.00	0.00	0.000	0	104.05	0.46	0.46	0.062	19
30.86	0.90	0.90	0.121	37	105.03	100.00	100.00	13.407	4095
33.83	0.37	0.37	0.049	15	106.04	18.56	18.56	2.488	760
33.85	0.29	0.29	0.039	12	107.04	1.15	1.15	0.154	47
33.94	0.34	0.34	0.046	14	119.01	0.71	0 71	0.095	29
36 11	0.46	0 46	0.062	19	119.96	35.16	35 16	4.715	1440
37.09	11 70	11.70	1.568	479	121.01	2.91	2 91	0.390	119
37.56	2.37	2.37	0 318	97	122.06	0.49	0.49	0.065	20
38.03	24.59	24.59	3.297	1007					
38.50	4.93	4.93	0.661	202					
38.96	31.23	31.23	4.188	1279					
39.80	0.15	0.15	0.020	6					
39.85	1.83	1.83	0.246	75					
40.93	3.13	3.13	0.419	128					
42.01	5.18	5.18	0.694	212					
43.07	68.74	68.74	9.217	2815					
44.09	0.22	0.22	0.029	9					
44.60	0.59	0.59	0.079	24					
45.62	1.22	1.22	0.164	50					
46.60	0.27	0.27	0.036	11					
48.01	0.24	0.24	0.033	10					
48.95	4.66	4.66	0.625	191					
49.87	49.99	49.99	6.702	2047					
50.93	99.78	99.78	13.378	4086					
52.01	14.63	14.63	1.961	599					
52.53	0.29	0.29	0.039	12					
53.06	1.22	1.22	0.164	50					
58.97	0.61	0.61	0.082	25					
59.88	0.44	0.44	0.059	18					
60.94	4.49	4.49	0.602	184					
62.00	5.96	5.96	0.799	244					
63.05	17.97	17.97	2.410	736					
64.08	15.60	15.60	2.092	639					
65.10	14.02	14.02	1.879	574					
66.10	1.39	1.39	0.187	57					
73.00	1.98	1.98	0.265	81					
74.04	10.94	10.94	1.467	448					
75.04	7.23	7.23	0.969	296					
76 04	8.96	8.96	1.202	367					
77.01	100 00	100.00	13.407	4095					
78.01	42.49	42.49	5.697	1740					
78.96	1.93	1.93	0.259	79					
86.02	0 29	0.29	0.039	12					
86.99	0.56	0.56	0.075	23					
87.98	0.83	0.83	0.111	34					
88.95	0 61	0.61	0.082	25					
89.90	0.71	0.71	0.095	29					
90.99	14.46	14.46	1.938	592					
91.64	0 27	0.27	0.036	11					

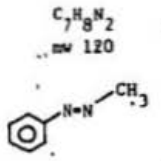


Table 12. Mass spectra of scan number 275 of condensed fraction.

AC3X4 306 RT 0 4 6 06-JUN-84 TIC=1495 AUTO-GAIN=1 2 1
CALGC1 BASE INT =4095 B/G SCAN=278 STATUS 1E
MSN1372 MPD PROD X4 LR EI GCMS

MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.	MASS	%HT. MOD.	%HT. BASE	% TIC	ABS HT.
22 14	0 32	0 32	0 074	13	95 08	0.46	0 46	0.108	19
25.31	0 37	0 37	0.085	15	101.99	0.22	0.22	0.051	9
26.27	1 37	1.37	0.318	56	103.02	0.42	0.42	0.097	17
27.21	4.03	4 03	0.938	165	104.04	0.27	0.27	0.063	11
28.09	0.00	0 00	0.000	0	105 04	8.79	8.79	2.047	360
29.82	0 27	0 27	0.063	11	106.05	0.81	0.81	0.188	33
30.86	0.02	0.02	0.006	1	118.01	0.83	0.83	0.193	34
34.10	0.29	0.29	0.068	12	118.98	0.44	0.44	0.102	18
36.09	0.27	0.27	0.063	11	119.97	1.86	1.86	0.432	76
36.12	0 37	0 37	0.085	15	130 89	0.32	0.32	0.074	13
37 09	2.95	2.95	0.688	121	180.94	0.22	0.22	0.051	9
38.03	7.62	7 62	1.774	312					
38.96	20.71	20.71	4.822	848					
39.80	0.12	0.12	0 028	5					
39.85	4.32	4.32	1.006	177					
40.93	6.15	6.15	1.433	252					
42.02	1.42	1.42	0.330	58					
43.08	1.25	1.25	0.290	51					
44.07	1.25	1.25	0.290	51					
45.62	4.32	4.32	1.006	177					
46.11	0.61	0.61	0.142	25					
46.61	13.85	13.85	3.224	567					
47.09	1.17	1.17	0.273	48					
48.96	1.22	1.22	0.284	50					
49.88	6.25	6.25	1.456	256					
50.94	10.16	10.16	2.365	416					
52.01	7.42	7.42	1.729	304					
53.07	2.34	2.34	0.546	96					
54.10	8.30	8.30	1.933	340					
55.12	0.66	0.66	0.154	27					
59.89	0.49	0.49	0.114	20					
60.95	2.52	2.52	0.586	103					
62.01	3.13	3.13	0.728	128					
63.06	7.79	7.79	1.814	319					
64.09	4.27	4.27	0.995	175					
65.11	37.41	37.41	8.711	1532					
66.09	68.74	68.74	16.006	2815					
67.07	6.64	6.64	1.547	272					
68.93	0 02	0.02	0.006	1					
73.01	0.54	0.54	0.125	22					
74 05	2 39	2.39	0.557	98					
76.05	2.20	2.20	0.512	90					
77 05	18.75	18.75	4.367	768					
78 02	6.72	6.72	1.564	275					
78.98	0.61	0.61	0.142	25					
87.01	0 27	0 27	0.063	11					
87.99	0.24	0.24	0.057	10					
88.95	0 29	0.29	0.068	12					
89.91	0 54	0.54	0.125	22					
90 96	2 91	2.91	0.677	119					
92.00	27 35	27.35	6.368	1120					
93.02	100.00	100 00	23.284	4095					
94.06	17.95	17.95	4.179	735					

C_7H_8N
mw 93

Table 33. Mass spectra of scan number 306 of condensed fraction.

Appendix C

Listed below are the analytical results of each of the kinetic runs. All runs give the initial conditions and the moles of products in the non-condensable fraction. In addition runs 100 to 158 give the calculated moles of products in the condensed fraction as outlined below.

The program below was written in basic on a Tandy 1200 computer to calculate the number of moles of each product in the condensed fraction for runs 100 to 158 in the unpacked vessel. The assumption for this calculation was that the condensed fraction for each run was all starting material.

The inputs for the program where the run number (RUNS), the time of the reaction (TIME), the temperature at which the reaction took place (TEMP), the number of moles per litre of 1-methyl-2-phenyldiazene (MPDA), the area of the peaks of products from the gas chromatograph, and the number of moles of nitrogen and methane from the non-condensable fraction.

The volume of liquid 1-methyl-2-phenyldiazene in μl is then calculated by

$$\text{LMPDA} = 120 * 1000 * \text{MPDA}/0.9851 \qquad (1)$$

where 120 is the molecular weight of 1-methyl-2-phenyldiazene; MPDA is the number of moles of reactant; 0.9851 is the density of 1-methyl-2-phenyldiazene in gm/ml; 1000 is the factor to convert from ml to μl.

The calibration factors of four products from the gas chromatograph response are then read. The fifth product in the condensable fraction, the mixed diazenes was not available, therefore the calibration factor was estimated by averaging the other four.

The number of moles of each product was then calculated by

$$\text{B(I)} = \text{A(I)} * \text{C(I)} * \text{LMPDA}/7 \qquad (2)$$

where B(I) was the number of moles of product; A(I) was the area of the gas chromatograph peak; C(I) was the calibration factor for the product LMPDA as defined above; 7 was the volume of condensed fraction in μl injected onto the gas chromatograph.

Below is a listing of the program and the results calculated for the runs which had data available.

Runs 1 to 75 were done using the packed vessel, volume 980.0 ml and the others were done using the unpacked vessel, volume 1007.4 ml, save for runs 218 to 230 which were in an unpacked vessel of 1,016 ml.

Moles of MPDA reported for runs 100 to 158 listed on the computer print-out are actually moles litre^{-1}.

```
10 REM "MATERIAL BALANCE  OF RUNS"
20 W = 1
30 READ RUNS,TIME,TEMP,MPDA
31 IF W = 5 THEN LPRINT CHR$(12)
32 IF W = 5 THEN W = 1
50 READ A(1),A(2),A(3),A(4),A(5)
70 READ A(6),A(7)
71 IF TEMP = 250 THEN TEMP = 519.2
72 IF TEMP =260 THEN TEMP = 529.4
73 IF TEMP = 270 THEN TEMP = 539.4
74 IF TEMP =280 THEN TEMP = 549.2
75 IF TEMP = 290 THEN TEMP = 559!
76 IF TEMP = 300 THEN TEMP = 568.8
80 LMPDA = 120*1000*MPDA/.9851
90 C(1) = 4E-08
92 C(2) = 5E-08
94 C(3) = 3E-08
96 C(4) = 3.5E-08
98 C(5) = 2.58E-08
100 FOR I = 1 TO 5
110 B(I) = A(I) * C(I)* LMPDA/7
120 NEXT I
130 BEN = B(1)*78
140 TOL =B(2)*92
150 ANIL = B(3)*93
160 DA  = B(4)*134
170 NMA =  B(5)*95
180 N2 = A(6)*28
190 CH4 = A(7)*16
200 BC = 72/78*BEN
210 BH = 6/78*BEN
220 TC = 84/92*TOL
230 TH = 8/92*TOL
240 AC = 72/93*ANIL
250 AH = 7/93*ANIL
260 AN = 14/93*ANIL
270 NC = 72/95*NMA
280 NH = 9/95*NMA
290 NN = 14/95*NMA
300 DC = 96/134*DA
310 DH = 10/134*DA
320 DN = 28/134*DA
330 CC = .75*CH4
340 CH = .25*CH4
350 TTC = BC+TC+AC+NC+DC+CC
360 TTH = BH+TH+AH+NH+DH+CH
370 TTN = AN+NN+DN+N2
380 LPRINT"RUN #" RUNS
390 LPRINT
400 LPRINT"TEMP " TEMP "          TIME" TIME
410 LPRINT
420 LPRINT "MPDA(moles)" MPDA
430 LPRINT
```

```
440 LPRINT
450 RCH = TTC/TTH
460 RCN = TTC/TTN
470 RNH = TTN/TTH
480 LPRINT "BENZENE(moles)              "B(1)
490 LPRINT "TOLUENE(moles)              "B(2)
500 LPRINT "ANILINE(moles)              "B(3)
510 LPRINT "N-METHYL ANILINE(moles)"B(5)
520 LPRINT "DIAZENES(moles)             "B(4)
530 LPRINT "NITROGEN(moles)             "A(6)
540 LPRINT "METHANE(moles)              "A(7)
550 LPRINT
560 LPRINT
690 W = W + 1
691 GOTO 30
710 DATA
100,600,290.0,1.979E-4,8.4,0,14.85,5.2,6.175,2.584E-6,
0.9011E-6
720 DATA
102,800.5,290.0,1.498E-4,4.3,0.14,29.9,7.25,8.94,3.542E-6,
0.9071E-6
730 DATA
103,900.4,290.0,1.527E-4,5.61,0.15,22.8,8.6,9.92,3.701E-6,
1.268E-6
740 DATA
104,1004.4,290.0,1.513E-4,3.36,1.95,5.1,5.17,8.68,3.338E-6,
1.422E-6
750 DATA
105,1000.6,290.0,1.518E-4,3.78,0.03,10.0,8.87,6.96,3.55E-6,
1.326E-6
760 DATA
106,1100.4,290.0,1.506E-4,5.3,0.18,20.68,9.84,9.3,3.927E-6,
1.539E-6
770 DATA
108,800.5,290.0,1.483E-4,3.96,0.04,23.32,6.09,8.4,3.410E-6,
1.002E-6
780 DATA
109,900.4,290.0,1.502E-4,2.91,0.16,8.64,6.00,6.6,3.246E-6,
1.198E-6
790 DATA
110,800.6,290.0,1.486E-4,3.315,0.03,14.4,6.00,7.26,2.500E-6,
1.002E-6
800 DATA
111,1212.2,290.0,1.485E-4,3.66,0.12,8.12,9.62,9.83,3.463E-6,
1.384E-6
810 DATA
112,800.3,290.0,1.497E-4,3.50,0.10,4.90,6.17,4.68,2.744E-6,
1.052E-6
820 DATA
113,1200.2,290.0,1.549E-4,3.42,0.09,8.56,9.97,7.90,3.615E-6,
1.279E-6
830 DATA
114,1200.2,290.0,1.503E-4,3.93,0.12,6.48,10.2,9.68,3.878E-6,
1.485E-6
```

```
840 DATA
117,1200,290.0,.0001561,4.16,0.11,5.25,9.26,11.96,41.09E-7,
15.15E-7
850 DATA
118,1200.8,290.0,1.488E-4,5.02,0.17,27.6,8.16,12.32,
4.850E-6,
1.609E-6
860 DATA
119,1300.8,290.0,1.478E-4,4.16,0.08,3.86,10.47,9.23,
4.246E-6,
1.842E-6
870 DATA
120,1300.9,290.0,1.498E-4,4.26,0.13,11.22,8.66,10.41,
4.498E-6,
1.848E-6
880 DATA
121,2001.0,260.0,0.680E-4,0.475,0,1.6,0.48,1.25,0.3047E-6,
0.04921E-6
890 DATA
122,2001.2,260.2,0.9427E-4,0.56,0,3.29,0.55,1.42,0.4420E-6,
0.07250E-6
900 DATA
123,2000.8,260.0,1.244E-4,0.58,0,5.50,1.47,3.99,0.7222E-6,
0.1017E-6
910 DATA
124,2000.7,260.0,1.853E-4,0.63,0,4.68,0.66,2.00,1.071E-6,
0.1536E-6
920 DATA
126,2000.7,260.0,2.457E-4,0.44,0,3.48,0.64,1.68,1.147E-6,
0.1788E-6
930 DATA
127,2000.3,260.0,3.122E-4,0.425,0,1.25,0.44,1.44,1.373E-6,
0.2482E-6
940 DATA
129,2000.5,260.0,3.67E-4,0.54,0,1.75,0.42,0.74,1.550E-6,
0.2767E-6
950 DATA
130,2000.9,260.0,6.916E-4,0.43,0,3.0,0.46,1.55,3.201E-6,
0.4345E-6
960 DATA
131,2000.5,260.0,4.321E-4,0.50,0,11.9,0.36,3.77,2.358E-6,
0.3165E-6
970 DATA
132,3000.4,260.0,1.552E-4,1.16,0,7.3,1.2,2.97,0.9146E-6,
0.1196E-6
980 DATA
133,1000.3,260.0,1.564E-4,0.35,0,1.48,0.30,0.50,0.3062E-6,
0.07830E-6
990 DATA
134,2000.2,260.0,1.561E-4,0.525,0,3.01,0.56,1.12,0.6100E-6,
0.1224E-6
1000 DATA
135,4000.4,260.0,1.557E-4,0.80,0,8.61,1.44,4.05,0.9852E-6,
0.1646E-6
```

```
1010 DATA
136,6000.0,260.0,1.543E-4,1.98,0.085,7.04,2.86,5.98,
1.930E-6,
0.4113E-6
1020 DATA
137,8000.3,260.0,1.566E-4,2.475,0.06,9.36,4.34,9.54,
2.625E-6,
0.5297E-6
1030 DATA
138,10400.3,260.0,1.561E-4,2.94,0.09,22.26,7.06,13.22,
3.287E-6,
.719E-6
1040 DATA
139,12000,260,1.54E-4,2.80,.03,26.18,7.82,15.08,3.596E-6,
.8009E-6
1050 DATA
140,4000.6,260,1.558E-4,1.29,0,6.56,2.34,4.35,1.253E-6,
0.2592E-6
1060 DATA
141,6000.3,250,1.464E-4,.90,.05,8.64,0.84,3.80,1.464E-6,
.9191E-6
1070 DATA
142,4000.3,250,2.500E-4,.51,0,2.64,.33,1.24,.8900E-6,
.1176E-6
1080 DATA
143,1800,270,2.247E-4,.99,0,1.44,1.5,2.49,2.061E-6,
.4979E-6
1090 DATA
144,1500,270,1.505E-4,.90,0,6.64,1.60,2.93,1.379E-6,
.2154E-6
1100 DATA
145,1800,270,1.508E-4,.99,.03,3.84,1.5,2.85,1.329E-6,
.2635E-6
1110 DATA
154,1800,270,1.696E-4,1.35,0,2.46,2.31,3.68,1.615E-6,
.4255E-6
1120 DATA
146,1800,280,1.479E-4,3.00,.09,9.25,6.57,7.5,3.091E-6,
.9251E-6
1130 DATA
147,1800,280,1.906E-4,3.26,.10,6.05,5.86,8.35,3.875E-6,
.9981E-6
1140 DATA
148,1800,280,1.589E-4,3.18,.06,21.06,6.94,9.68,3.637E-6,
.9053E-6
1150 DATA
155,1800,280,1.598E-4,3.17,.09,4.66,5.74,7.32,3.088E-6,
1.147E-6
1160 DATA
156,1800,280,1.969E-4,2.98,.06,3.24,5.75,7.49,3.856E-6,
1.422E-6
1170 DATA
157,600,300,1.431E-4,5.83,.18,3.94,10.72,9.67,4.087E-6,
2.106E-6
```

LEAF 122 OMITTED IN PAGE NUMBERING

```
1180 DATA
158,600,300,1.690E-4,5.11,.18,3.64,8.00,9.62,4.963E-6,
2.371E-6
1200 END
```

RUN # 1

TEMP(K) 559.0 TIME(s) 730.8

MPDA (mol/L) 0.00002318

NITROGEN (moles) 0.3431E-6
METHANE (moles) 0.05640E-6

RUN # 3

TEMP(K) 559.0 TIME(s) 1722.0

MPDA (mol/L) 0.0001073

NITROGEN (moles) 3.947E-6
METHANE (moles) 1.159E-6

RUN # 4

TEMP(K) 559.0 TIME(s) 1729.0

MPDA (mol/L) 0.0001085

NITROGEN (moles) 4.191E-6
METHANE (moles) 1.228E-6

RUN # 8

TEMP(K) 559.0 TIME(s) 1012.0

MPDA (mol/L) 0.0002339

NITROGEN (moles) 5.734E-6
METHANE (moles) 1.696E-6

RUN # 9

TEMP(K) 559.0 TIME(s) 1007.0

MPDA (mol/L) 0.0001796

NITROGEN (moles) 4.603E-6
METHANE (moles) 1.838E-6

RUN # 11

TEMP(K) 559.0 TIME(s) 1013.0

MPDA (mol/L) 0.00006728

NITROGEN (moles) 2.113E-6
METHANE (moles) 0.5733E-6

RUN # 15

TEMP(K) 559.0 TIME(s) 1012.2

MPDA (mol/L) 0.0001556

NITROGEN (moles) 3.658E-6
METHANE (moles) 1.011E-6

RUN # 17

TEMP(K) 568.8 TIME(s) 613.1

MPDA (mol/L) 0.0001325

NITROGEN (moles) 4.484E-6
METHANE (moles) 0.9220E-6

RUN # 18

TEMP(K) 568.8 TIME(s) 608.0

MPDA (mol/L) 0.0001665

NITROGEN (moles) 5.228E-6
METHANE (moles) 1.640E-6

RUN # 19

TEMP(K) 568.8 TIME(s) 607.3

MPDA (mol/L) 0.0001011

NITROGEN (moles) 3.568E-6
METHANE (moles) 0.8130E-6

RUN # 20

TEMP(K) 568.8 TIME(s) 608.9

MPDA (mol/L) 0.00004492

NITROGEN (moles) 1.396E-6
METHANE (moles) 0.5047E-6

RUN # 21

TEMP(K) 568.8 TIME(s) 608.9

MPDA (mol/L) 0.00004907

NITROGEN (moles) 2.003E-6
METHANE (moles) 0.5362E-6

RUN # 60

TEMP(K) 568.8 TIME(s) 607.1

MPDA (mol/L) 0.0001435

NITROGEN (moles) 4.300E-6
METHANE (moles) 1.057E-6

RUN # 61

TEMP(K) 568.8 TIME(s) 604.6

MPDA (mol/L) 0.00007249

NITROGEN (moles) 2.256E-6
METHANE (moles) 0.6468E-6

RUN # 25

TEMP(K) 519.2 TIME(s) 5012.5

MPDA (mol/L) 0.0001438

NITROGEN (moles) 1.172E-6
METHANE (moles) 0.08794E-6

RUN # 27

TEMP(K) 529.4 TIME(s) 7214.5

MPDA (mol/L) 0.0001337

NITROGEN (moles) 2.120E-6
METHANE (moles) 0.1813E-6

RUN # 28

TEMP(K) 529.4 TIME(s) 11019.8

MPDA (mol/L) 0.0001604

NITROGEN (moles) 3.459E-6
METHANE (moles) 0.3467E-6

RUN # 29

TEMP(K) 529.4 TIME(s) 15411.5

MPDA (mol/L) 0.0001577

NITROGEN (moles) 5.240E-6
METHANE (moles) 0.6226E-6

RUN # 31

TEMP(K) 529.4 TIME(s) 3620.0

MPDA (mol/L) 0.0001544

NITROGEN (moles) 1.765E-6
METHANE (moles) 0.1418E-6

RUN # 32

TEMP(K) 529.4 TIME(s) 3611.5

MPDA (mol/L) 0.0001530

NITROGEN (moles) 1.702E-6
METHANE (moles) 0.1103E-6

RUN # 35

TEMP(K) 529.4 TIME(s) 3615.7

MPDA (mol/L) 0.0001590

NITROGEN (moles) 1.571E-6
METHANE (moles) 0.1263E-6

RUN # 36

TEMP(K) 529.4 TIME(s) 1815.7

MPDA (mol/L) 0.0001590

NITROGEN (moles) 0.7538E-6
METHANE (moles) 0.07830E-6

RUN # 39

TEMP(K) 529.4 TIME(s) 1809.8

MPDA (mol/L) 0.0001560

NITROGEN (moles) 0.6748E-6
METHANE (moles) 0.04903E-6

RUN # 40

TEMP(K) 529.4 TIME(s) 1814.8

MPDA (mol/L) 0.0001541

NITROGEN (moles) 1.387E-6
METHANE (moles) 0.08669E-6

RUN # 45

TEMP(K) 529.4 TIME(s) 1809.5

MPDA (mol/L) 0.0001604

NITROGEN (moles) 1.377E-6
METHANE (moles) 0.03129E-6

RUN # 46

TEMP(K) 529.4 TIME(s) 1812.1

MPDA (mol/L) 0.0001854

NITROGEN (moles) 1.309E-6
METHANE (moles) 0.02950E-6

RUN # 47

TEMP(K) 529.4 TIME(s) 1811.6

MPDA (mol/L) 0.0001556

NITROGEN (moles) 1.081E-6
METHANE (moles) 0.03477E-6

RUN # 48

TEMP(K) 529.4 TIME(s) 1821.5

MPDA (mol/L) 0.0001553

NITROGEN (moles) 1.360E-6
METHANE (moles) 0.02806E-6

RUN # 49

TEMP(K) 529.4 TIME(s) 3609.8

MPDA (mol/L) 0.0001668

NITROGEN (moles) 2.862E-6
METHANE (moles) 0.05535E-6

RUN # 50

TEMP(K) 529.4 TIME(s) 3622.2

MPDA (mol/L) 0.0002737

NITROGEN (moles) 4.074E-6
METHANE (moles) 0.1103E-6

RUN # 51

TEMP(K) 529.4 TIME(s) 7015.6

MPDA (mol/L) 0.0001585

NITROGEN (moles) 3.846E-6
METHANE (moles) 0.1576E-6

RUN # 52

TEMP(K) 529.4 TIME(s) 7012.6

MPDA (mol/L) 0.0001638

NITROGEN (moles) 3.885E-6
METHANE (moles) 0.1891E-6

RUN # 53

TEMP(K) 529.4 TIME(s) 5019.1

MPDA (mol/L) 0.0001576

NITROGEN (moles) 2.703E-6
METHANE (moles) 0.1418E-6

RUN # 54

TEMP(K) 529.4 TIME(s) 5005.2

MPDA (mol/L) 0.0001564

NITROGEN (moles) 3.086E-6
METHANE (moles) 0.1723E-6

RUN # 55

TEMP(K) 529.4 TIME(s) 1810.9

MPDA (mol/L) 0.0001553

NITROGEN (moles) 1.307E-6
METHANE (moles) 0.05804E-6

RUN # 56

TEMP(K) 529.4 TIME(s) 12010.2

MPDA (mol/L) 0.0001568

NITROGEN (moles) 5.337E-6
METHANE (moles) 0.3795E-6

RUN # 57

TEMP(K) 529.4 TIME(s) 15011.1

MPDA (mol/L) 0.0001584

NITROGEN (moles) 5.986E-6
METHANE (moles) 0.5333E-6

RUN # 58

TEMP(K) 529.4 TIME(s) 6504.1

MPDA (mol/L) 0.0001619

NITROGEN (moles) 3.050E-6
METHANE (moles) 0.2522E-6

RUN # 59

TEMP(K) 529.4 TIME(s) 3010.7

MPDA (mol/L) 0.0002669

NITROGEN (moles) 2.671E-6
METHANE (moles) 0.2193E-6

RUN # 71

TEMP(K) 529.4 TIME(s) 8204.7

MPDA (mol/L) 0.0003793

NITROGEN (moles) 11.51E-6
METHANE (moles) 1.033E-6

RUN # 72

TEMP(K) 529.4 TIME(s) 1806.5

MPDA (mol/L) 0.0007825

NITROGEN (moles) 4.078E-6
METHANE (moles) 0.2445E-6

RUN # 73

TEMP(K) 529.4 TIME(s) 3608.1

MPDA (mol/L) 0.0007155

NITROGEN (moles) 10.60E-6
METHANE (moles) 0.6842E-6

RUN # 74

TEMP(K) 529.4 TIME(s) 2409.5

MPDA (mol/L) 0.0004586

NITROGEN (moles) 6.651E-6
METHANE (moles) 0.2922E-6

RUN # 75

TEMP(K) 529.4 TIME(s) 2406.1

MPDA (mol/L) 0.0007261

NITROGEN (moles) 5.445E-6
METHANE (moles) 0.3725E-6

RUN # 63

TEMP(K) 549.6 TIME(s) 1510.9

MPDA (mol/L) 0.0001536

NITROGEN (moles) 3.313E-6
METHANE (moles) 0.4349E-6

RUN # 64

TEMP(K) 549.6 TIME(s) 1206.4

MPDA (mol/L) 0.001188

NITROGEN (moles) 20.00E-6
METHANE (moles) 3.271E-6

RUN # 65

TEMP(K) 549.7 TIME(s) 906.1

MPDA (mol/L) 0.001140

NITROGEN (moles) 16.81E-6
METHANE (moles) 2.778E-6

RUN # 68

TEMP(K) 539.4 TIME(s) 2108.5

MPDA (mol/L) 0.0001557

NITROGEN (moles) 2.252E-6
METHANE (moles) 0.2844E-6

RUN # 69

TEMP(K) 539.4 TIME(s) 1810.5

MPDA (mol/L) 0.001082

NITROGEN (moles) 12.69E-6
METHANE (moles) 1.916E-6

RUN # 70

TEMP(K) 539.4 TIME(s) 1804.9

MPDA (mol/L) 0.0009150

NITROGEN (moles) 10.46E-6
METHANE (moles) 1.3233E-6

RUN # 76

TEMP(K) 559.0 TIME(s) 1009.4

MPDA (mol/L) 0.0001148

NITROGEN (moles) 2.584E-6
METHANE (moles) 0.9011E-6

RUN # 77

TEMP(K) 559.0 TIME(s) 1005.1

MPDA (mol/L) 0.0001578

NITROGEN (moles) 3.256E-6
METHANE (moles) 1.783E-6

RUN # 78

TEMP(K) 559.0 TIME(s) 1002.6

MPDA (mol/L) 0.0001396

NITROGEN (moles) 3.116E-6
METHANE (moles) 1.554E-6

RUN # 79

TEMP(K) 559.0 TIME(s) 1001.3

MPDA (mol/L) 0.0001220

NITROGEN (moles) 2.870E-6
METHANE (moles) 1.312E-6

RUN # 83

TEMP(K) 559.0 TIME(s) 1001.6

MPDA (mol/L) 0.0001764

NITROGEN (moles) 4.466E-6
METHANE (moles) 1.404E-6

RUN # 85

TEMP(K) 559.0 TIME(s) 1026.7

MPDA (mol/L) 0.0002110

NITROGEN (moles) 4.210E-6
METHANE (moles) 1.627E-6

RUN # 86

TEMP(K) 559.0 TIME(s) 1001.4

MPDA (mol/L) 0.0002482

NITROGEN (moles) 5.550E-6
METHANE (moles) 2.135E-6

RUN # 87

TEMP(K) 559.0 TIME(s) 1001.1

MPDA (mol/L) 0.0001816

NITROGEN (moles) 3.684E-6
METHANE (moles) 1.300E-6

RUN # 88

TEMP(K) 559.0 TIME(s) 1001.1

MPDA (mol/L) 0.0001602

NITROGEN (moles) 4.191E-6
METHANE (moles) 1.494E-6

RUN # 89

TEMP(K) 559.0 TIME(s) 1000.9

MPDA (mol/L) 0.0001375

NITROGEN (moles) 3.304E-6
METHANE (moles) 1.241E-6

RUN # 90

TEMP(K) 559.0 TIME(s) 1001.1

MPDA (mol/L) 0.0001174

NITROGEN (moles) 2.867E-6
METHANE (moles) 1.003E-6

RUN # 91

TEMP(K) 559.0 TIME(s) 1000.7

MPDA (mol/L) 0.00009771

NITROGEN (moles) 2.404E-6
METHANE (moles) 0.8697E-6

RUN # 92

TEMP(K) 559.0 TIME(s) 1001.0

MPDA (mol/L) 0.00008360

NITROGEN (moles) 1.658E-6
METHANE (moles) 0.5525E-6

RUN # 93

TEMP(K) 559.0 TIME(s) 1000.7

MPDA (mol/L) 0.00007146

NITROGEN (moles) 1.664E-6
METHANE (moles) 0.6151E-6

RUN # 94

TEMP(K) 559.0 TIME(s) 1000.6

MPDA (mol/L) 0.00004294

NITROGEN (moles) 1.042E-6
METHANE (moles) 0.2943E-6

RUN # 95

TEMP(K) 559.0 TIME(s) 1000.4

MPDA (mol/L) 0.0003776

NITROGEN (moles) 9.933E-6
METHANE (moles) 4.043E-6

RUN # 96

TEMP(K) 559.0 TIME(s) 1000.7

MPDA (mol/L) 0.0002520

NITROGEN (moles) 6.940E-6
METHANE (moles) 2.127E-6

RUN # 97

TEMP(K) 559.0 TIME(s) 1000.9

MPDA (mol/L) 0.0005522

NITROGEN (moles) 13.46E-6
METHANE (moles) 5.647E-6

RUN # 99

TEMP(K) 559.0 TIME(s) 600.3

MPDA (mol/L) 0.0001484

NITROGEN (moles) 1.953E-6
METHANE (moles) 0.6325E-6

RUN # 202

TEMP(K) 549.8 TIME(s) 903.3

MPDA (mol/L) 0.0004742

NITROGEN (moles) 4.789E-6
METHANE (moles) 1.748E-6

RUN # 203

TEMP(K) 519.2 TIME(s) 7549.6

MPDA (mol/L) 0.0001767

NITROGEN (moles) 1.172E-6
METHANE (moles) 0.09421E-6

RUN # 205

TEMP(K) 568.8 TIME(s) 600.2

MPDA (mol/L) 0.0001483

NITROGEN (moles) 3.939E-6
METHANE (moles) 1.598E-6

RUN # 206

TEMP(K) 559.0 TIME(s) 1000.1

MPDA (mol/L) 0.0005931

NITROGEN (moles) 15.72E-6
METHANE (moles) 6.377E-6

RUN # 207

TEMP(K) 559.0 TIME(s) 1000.1

MPDA (mol/L) 0.0009145

NITROGEN (moles) 25.87E-6
METHANE (moles) 8.192E-6

RUN # 208

TEMP(K) 559.0 TIME(s) 1000.2

MPDA (mol/L) 0.001044

NITROGEN (moles) 29.78E-6
METHANE (moles) 9.454E-6

RUN # 100

TEMP 559 TIME 600

MPDA(moles) .0001979

BENZENE(moles)	1.157145E-06
TOLUENE(moles)	0
ANILINE(moles)	1.534251E-06
N-METHYL ANILINE(moles)	5.486627E-07
DIAZENES(moles)	6.267871E-07
NITROGEN(moles)	2.584E-06
METHANE(moles)	9.011E-07

RUN # 102

TEMP 559 TIME 800.5

MPDA(moles) .0001498

BENZENE(moles)	4.483768E-07
TOLUENE(moles)	1.824789E-08
ANILINE(moles)	2.338337E-06
N-METHYL ANILINE(moles)	6.012733E-07
DIAZENES(moles)	6.614862E-07
NITROGEN(moles)	3.542E-06
METHANE(moles)	9.071E-07

RUN # 103

TEMP 559 TIME 900.4

MPDA(moles) .0001527

BENZENE(moles)	5.962999E-07
TOLUENE(moles)	1.992981E-08
ANILINE(moles)	1.817599E-06
N-METHYL ANILINE(moles)	6.801009E-07
DIAZENES(moles)	7.998497E-07
NITROGEN(moles)	3.701E-06
METHANE(moles)	1.268E-06

RUN # 104

TEMP 559 TIME 1004.4

MPDA(moles) .0001513

BENZENE(moles)	3.538678E-07
TOLUENE(moles)	2.567122E-07
ANILINE(moles)	4.028406E-07
N-METHYL ANILINE(moles)	5.896323E-07
DIAZENES(moles)	4.764315E-07
NITROGEN(moles)	3.338E-06
METHANE(moles)	1.422E-06

RUN # 105

TEMP 559 TIME 1000.6

MPDA(moles) .0001518

BENZENE(moles)	3.994169E-07
TOLUENE(moles)	3.96247E-09
ANILINE(moles)	7.924938E-07
N-METHYL ANILINE(moles)	4.743552E-07
DIAZENES(moles)	8.200991E-07
NITROGEN(moles)	3.55E-06
METHANE(moles)	1.326E-06

RUN # 106

TEMP 559 TIME 1100.4

MPDA(moles) .0001506

BENZENE(moles)	5.556019E-07
TOLUENE(moles)	2.358688E-08
ANILINE(moles)	1.625922E-06
N-METHYL ANILINE(moles)	6.28826E-07
DIAZENES(moles)	9.02591E-07
NITROGEN(moles)	3.927E-06
METHANE(moles)	1.539E-06

RUN # 108

TEMP 559 TIME 800.5

MPDA(moles) .0001483

BENZENE(moles)	4.08789E-07
TOLUENE(moles)	5.161477E-09
ANILINE(moles)	1.805485E-06
N-METHYL ANILINE(moles)	5.592977E-07
DIAZENES(moles)	5.500844E-07
NITROGEN(moles)	3.41E-06
METHANE(moles)	1.002E-06

RUN # 109

TEMP 559 TIME 900.4

MPDA(moles) .0001502

BENZENE(moles)	3.042466E-07
TOLUENE(moles)	2.091042E-08
ANILINE(moles)	6.774976E-07
N-METHYL ANILINE(moles)	4.450783E-07
DIAZENES(moles)	5.488986E-07
NITROGEN(moles)	3.246E-06
METHANE(moles)	1.198E-06

RUN # 110

TEMP 559 TIME 800.6

MPDA(moles) .0001486

BENZENE(moles)	3.428982E-07
TOLUENE(moles)	3.878939E-09
ANILINE(moles)	1.117134E-06
N-METHYL ANILINE(moles)	4.843709E-07
DIAZENES(moles)	5.430515E-07
NITROGEN(moles)	.0000025
METHANE(moles)	1.002E-06

RUN # 111

TEMP 559 TIME 1212.2

MPDA(moles) .0001485

BENZENE(moles)	3.783297E-07
TOLUENE(moles)	1.550532E-08
ANILINE(moles)	6.295158E-07
N-METHYL ANILINE(moles)	6.553942E-07
DIAZENES(moles)	8.701064E-07
NITROGEN(moles)	3.463E-06
METHANE(moles)	1.384E-06

RUN # 112

TEMP 559 TIME 800.3

MPDA(moles) .0001497

BENZENE(moles)	3.647143E-07
TOLUENE(moles)	1.302551E-08
ANILINE(moles)	3.8295E-07
N-METHYL ANILINE(moles)	3.145504E-07
DIAZENES(moles)	5.625718E-07
NITROGEN(moles)	2.744E-06
METHANE(moles)	1.052E-06

RUN # 113

TEMP 559 TIME 1200.2

MPDA(moles) .0001549

BENZENE(moles)	3.687571E-07
TOLUENE(moles)	1.213017E-08
ANILINE(moles)	6.922283E-07
N-METHYL ANILINE(moles)	5.494158E-07
DIAZENES(moles)	9.406272E-07
NITROGEN(moles)	3.615E-06
METHANE(moles)	1.279E-06

RUN # 114

TEMP 559 TIME 1200.2

MPDA(moles) .0001503

BENZENE(moles)	4.111634E-07
TOLUENE(moles)	1.569326E-08
ANILINE(moles)	5.084616E-07
N-METHYL ANILINE(moles)	6.532162E-07
DIAZENES(moles)	9.337488E-07
NITROGEN(moles)	3.878E-06
METHANE(moles)	1.485E-06

RUN # 117

TEMP 559 TIME 1200

MPDA(moles) .0001561

BENZENE(moles)	4.520215E-07
TOLUENE(moles)	1.494061E-08
ANILINE(moles)	4.278449E-07
N-METHYL ANILINE(moles)	8.382175E-07
DIAZENES(moles)	8.804096E-07
NITROGEN(moles)	4.109E-06
METHANE(moles)	1.515E-06

RUN # 118

TEMP 559 TIME 1200.8

MPDA(moles) .0001488

BENZENE(moles)	5.199595E-07
TOLUENE(moles)	2.201024E-08
ANILINE(moles)	2.144056E-06
N-METHYL ANILINE(moles)	8.23069E-07
DIAZENES(moles)	7.395439E-07
NITROGEN(moles)	4.85E-06
METHANE(moles)	1.609E-06

RUN # 119

TEMP 559 TIME 1300.8

MPDA(moles) .0001478

BENZENE(moles)	4.279871E-07
TOLUENE(moles)	1.028815E-08
ANILINE(moles)	2.97842E-07
N-METHYL ANILINE(moles)	6.124897E-07
DIAZENES(moles)	9.425233E-07
NITROGEN(moles)	4.246E-06
METHANE(moles)	1.842E-06

RUN # 120

TEMP 559 TIME 1300.9

MPDA(moles) .0001498

BENZENE(moles)	4.442059E-07
TOLUENE(moles)	1.694447E-08
ANILINE(moles)	8.774631E-07
N-METHYL ANILINE(moles)	7.001404E-07
DIAZENES(moles)	7.901338E-07
NITROGEN(moles)	4.498E-06
METHANE(moles)	1.848E-06

RUN # 121

TEMP 529.4 TIME 2001

MPDA(moles) .000068

BENZENE(moles)	2.248358E-08
TOLUENE(moles)	0
ANILINE(moles)	5.680062E-08
N-METHYL ANILINE(moles)	3.816291E-08
DIAZENES(moles)	1.988022E-08
NITROGEN(moles)	3.047E-07
METHANE(moles)	4.921E-08

RUN # 122

TEMP 260.2 TIME 2001.2

MPDA(moles) 9.427E-05

BENZENE(moles)	3.674722E-08
TOLUENE(moles)	0
ANILINE(moles)	1.619174E-07
N-METHYL ANILINE(moles)	6.010138E-08
DIAZENES(moles)	3.157964E-08
NITROGEN(moles)	4.42E-07
METHANE(moles)	7.25E-08

RUN # 123

TEMP 529.4 TIME 2000.8

MPDA(moles) .0001244

BENZENE(moles)	5.0224E-08
TOLUENE(moles)	0
ANILINE(moles)	3.571965E-07
N-METHYL ANILINE(moles)	2.228517E-07
DIAZENES(moles)	1.113804E-07
NITROGEN(moles)	7.222E-07
METHANE(moles)	1.017E-07

RUN # 124

TEMP 529.4 TIME 2000.7

MPDA(moles) .0001853

BENZENE(moles)	8.126038E-08
TOLUENE(moles)	0
ANILINE(moles)	4.527364E-07
N-METHYL ANILINE(moles)	1.663903E-07
DIAZENES(moles)	7.448869E-08
NITROGEN(moles)	1.071E-06
METHANE(moles)	1.536E-07

RUN # 126

TEMP 529.4 TIME 2000.7

MPDA(moles) .0002457

BENZENE(moles)	7.525246E-08
TOLUENE(moles)	0
ANILINE(moles)	4.463839E-07
N-METHYL ANILINE(moles)	1.853263E-07
DIAZENES(moles)	9.577586E-08
NITROGEN(moles)	1.147E-06
METHANE(moles)	1.788E-07

RUN # 127

TEMP 529.4 TIME 2000.3

MPDA(moles) .0003122

BENZENE(moles)	9.236016E-08
TOLUENE(moles)	0
ANILINE(moles)	2.037356E-07
N-METHYL ANILINE(moles)	2.01845E-07
DIAZENES(moles)	8.366744E-08
NITROGEN(moles)	1.373E-06
METHANE(moles)	2.482E-07

RUN # 129

TEMP 529.4 TIME 2000.5

MPDA(moles) .000367

BENZENE(moles)	1.379503E-07
TOLUENE(moles)	0
ANILINE(moles)	3.352959E-07
N-METHYL ANILINE(moles)	1.219328E-07
DIAZENES(moles)	9.388286E-08
NITROGEN(moles)	1.55E-06
METHANE(moles)	2.767E-07

RUN # 130

TEMP 529.4 TIME 2000.9

MPDA(moles) 6.916001E-04

BENZENE(moles)	2.070076E-07
TOLUENE(moles)	0
ANILINE(moles)	1.083179E-06
N-METHYL ANILINE(moles)	4.812927E-07
DIAZENES(moles)	1.937688E-07
NITROGEN(moles)	3.201E-06
METHANE(moles)	4.345E-07

RUN # 131

TEMP 529.4 TIME 2000.5

MPDA(moles) .0004321

BENZENE(moles)	1.503894E-07
TOLUENE(moles)	0
ANILINE(moles)	2.68445E-06
N-METHYL ANILINE(moles)	7.313887E-07
DIAZENES(moles)	9.474531E-08
NITROGEN(moles)	2.358E-06
METHANE(moles)	3.165E-07

RUN # 132

TEMP 529.4 TIME 3000.4

MPDA(moles) .0001552

BENZENE(moles)	1.253178E-07
TOLUENE(moles)	0
ANILINE(moles)	5.914783E-07
N-METHYL ANILINE(moles)	2.069526E-07
DIAZENES(moles)	1.134342E-07
NITROGEN(moles)	9.146E-07
METHANE(moles)	1.196E-07

RUN # 133

TEMP 529.4 TIME 1000.3

MPDA(moles) .0001564

BENZENE(moles)	3.810374E-08
TOLUENE(moles)	0
ANILINE(moles)	1.208433E-07
N-METHYL ANILINE(moles)	3.510988E-08
DIAZENES(moles)	2.857781E-08
NITROGEN(moles)	3.062E-07
METHANE(moles)	7.83E-08

RUN # 134

TEMP 529.4 TIME 2000.2

MPDA(moles) .0001561

BENZENE(moles)	5.704598E-08
TOLUENE(moles)	0
ANILINE(moles)	2.452977E-07
N-METHYL ANILINE(moles)	7.849527E-08
DIAZENES(moles)	5.324292E-08
NITROGEN(moles)	6.1E-07
METHANE(moles)	1.224E-07

RUN # 135

TEMP 529.4 TIME 4000.4

MPDA(moles) .0001557

BENZENE(moles)	8.670447E-08
TOLUENE(moles)	0
ANILINE(moles)	6.998676E-07
N-METHYL ANILINE(moles)	2.831172E-07
DIAZENES(moles)	1.365595E-07
NITROGEN(moles)	9.852E-07
METHANE(moles)	1.646E-07

RUN # 136

TEMP 529.4 TIME 6000

MPDA(moles) .0001543

BENZENE(moles)	2.12664E-07
TOLUENE(moles)	1.141189E-08
ANILINE(moles)	5.67104E-07
N-METHYL ANILINE(moles)	4.14276E-07
DIAZENES(moles)	2.687837E-07
NITROGEN(moles)	1.93E-06
METHANE(moles)	4.113E-07

RUN # 137

TEMP 529.4 TIME 8000.3

MPDA(moles) .0001566

BENZENE(moles)	2.697925E-07
TOLUENE(moles)	8.175531E-09
ANILINE(moles)	7.652296E-07
N-METHYL ANILINE(moles)	6.707532E-07
DIAZENES(moles)	4.139543E-07
NITROGEN(moles)	2.625E-06
METHANE(moles)	5.297E-07

RUN # 138

TEMP 529.4 TIME 10400.3

MPDA(moles) .0001561

BENZENE(moles)	3.194575E-07
TOLUENE(moles)	1.222414E-08
ANILINE(moles)	1.814062E-06
N-METHYL ANILINE(moles)	9.265245E-07
DIAZENES(moles)	6.712411E-07
NITROGEN(moles)	3.287E-06
METHANE(moles)	7.19E-07

RUN # 139

TEMP 529.4 TIME 12000

MPDA(moles) .000154

BENZENE(moles)	3.001523E-07
TOLUENE(moles)	4.019897E-09
ANILINE(moles)	2.104818E-06
N-METHYL ANILINE(moles)	1.042665E-06
DIAZENES(moles)	7.334972E-07
NITROGEN(moles)	3.596E-06
METHANE(moles)	8.009E-07

RUN # 140

TEMP 529.4 TIME 4000.6

MPDA(moles) .0001558

BENZENE(moles)	1.399007E-07
TOLUENE(moles)	0
ANILINE(moles)	5.335749E-07
N-METHYL ANILINE(moles)	3.042841E-07
DIAZENES(moles)	2.220518E-07
NITROGEN(moles)	1.253E-06
METHANE(moles)	2.592E-07

RUN # 141

TEMP 519.2 TIME 6000.3

MPDA(moles) .0001464

BENZENE(moles)	9.171628E-08
TOLUENE(moles)	6.369187E-09
ANILINE(moles)	6.603572E-07
N-METHYL ANILINE(moles)	2.497?4E-07
DIAZENES(moles)	7.490162E-08
NITROGEN(moles)	1.464E-06
METHANE(moles)	9.191E-07

RUN # 142

TEMP 519.2 TIME 4000.3

MPDA(moles) .00025

BENZENE(moles)	8.875098E-08
TOLUENE(moles)	0
ANILINE(moles)	3.445626E-07
N-METHYL ANILINE(moles)	1.391824E-07
DIAZENES(moles)	5.024871E-08
NITROGEN(moles)	8.9E-07
METHANE(moles)	1.176E-07

RUN # 143

TEMP 539.4 TIME 1800

MPDA(moles) .0002247

BENZENE(moles)	1.548464E-07
TOLUENE(moles)	0
ANILINE(moles)	1.689234E-07
N-METHYL ANILINE(moles)	2.512031E-07
DIAZENES(moles)	2.052888E-07
NITROGEN(moles)	2.061E-06
METHANE(moles)	4.979E-07

RUN # 144

TEMP 539.4 TIME 1500

MPDA(moles) .0001505

BENZENE(moles)	9.428484E-08
TOLUENE(moles)	0
ANILINE(moles)	5.217095E-07
N-METHYL ANILINE(moles)	1.979825E-07
DIAZENES(moles)	1.466653E-07
NITROGEN(moles)	1.379E-06
METHANE(moles)	2.154E-07

RUN # 145

TEMP 539.4 TIME 1800

MPDA(moles) .0001508

BENZENE(moles)	1.039201E-07
TOLUENE(moles)	3.936366E-09
ANILINE(moles)	3.023129E-07
N-METHYL ANILINE(moles)	1.929607E-07
DIAZENES(moles)	1.377728E-07
NITROGEN(moles)	1.329E-06
METHANE(moles)	2.635E-07

RUN # 154

TEMP 539.4 TIME 1800

MPDA(moles) .0001696

BENZENE(moles)	1.593759E-07
TOLUENE(moles)	0
ANILINE(moles)	2.178137E-07
N-METHYL ANILINE(moles)	2.802181E-07
DIAZENES(moles)	2.38621E-07
NITROGEN(moles)	1.615E-06
METHANE(moles)	4.255E-07

RUN # 146

TEMP 549.2 TIME 1800

MPDA(moles) .0001479

BENZENE(moles)	3.088534E-07
TOLUENE(moles)	1.1582E-08
ANILINE(moles)	7.142234E-07
N-METHYL ANILINE(moles)	4.980261E-07
DIAZENES(moles)	5.918403E-07
NITROGEN(moles)	3.091E-06
METHANE(moles)	9.251E-07

RUN # 147

TEMP 549.2 TIME 1800

MPDA(moles) .0001906

BENZENE(moles)	4.325172E-07
TOLUENE(moles)	1.658425E-08
ANILINE(moles)	6.020082E-07
N-METHYL ANILINE(moles)	7.14549E-07
DIAZENES(moles)	6.802858E-07
NITROGEN(moles)	3.875E-06
METHANE(moles)	9.980999E-07

RUN # 148

TEMP 549.2 TIME 1800

MPDA(moles) .0001589

BENZENE(moles)	3.517336E-07
TOLUENE(moles)	8.295605E-09
ANILINE(moles)	1.747054E-06
N-METHYL ANILINE(moles)	6.905925E-07
DIAZENES(moles)	6.716674E-07
NITROGEN(moles)	3.637E-06
METHANE(moles)	9.053E-07

RUN # 155

TEMP 549.2 TIME 1800

MPDA(moles) .0001598

BENZENE(moles)	3.526135E-07
TOLUENE(moles)	1.251389E-08
ANILINE(moles)	3.887647E-07
N-METHYL ANILINE(moles)	5.251828E-07
DIAZENES(moles)	5.586754E-07
NITROGEN(moles)	3.088E-06
METHANE(moles)	1.147E-06

RUN # 156

TEMP 549.2 TIME 1800

MPDA(moles) .0001969

BENZENE(moles)	4.084368E-07
TOLUENE(moles)	1.027945E-08
ANILINE(moles)	3.330542E-07
N-METHYL ANILINE(moles)	6.621405E-07
DIAZENES(moles)	6.895798E-07
NITROGEN(moles)	3.856E-06
METHANE(moles)	1.422E-06

RUN # 157

TEMP 568.8 TIME 600

MPDA(moles) .0001431

BENZENE(moles)	5.807257E-07
TOLUENE(moles)	2.241223E-08
ANILINE(moles)	2.943473E-07
N-METHYL ANILINE(moles)	6.212819E-07
DIAZENES(moles)	9.343408E-07
NITROGEN(moles)	4.087E-06
METHANE(moles)	2.106E-06

RUN # 158

TEMP 568.8 TIME 600

MPDA(moles) .000169

BENZENE(moles)	6.01133E-07
TOLUENE(moles)	2.646867E-08
ANILINE(moles)	3.211532E-07
N-METHYL ANILINE(moles)	7.299353E-07
DIAZENES(moles)	8.234698E-07
NITROGEN(moles)	4.963E-06
METHANE(moles)	2.371E-06

RUN # 159

TEMP(K) 559.0 TIME(s) 1000.2

MPDA (mol/L) 0.00002604 PROPENE : DIAZENE 85.2 : 1

NITROGEN (moles) 0.6583E-6
METHANE (moles) 0.1160E-6

RUN # 160

TEMP(K) 559.0 TIME(s) 1000.1

MPDA (mol/L) 0.00002222 PROPENE : DIAZENE 85.2 : 1

NITROGEN (moles) 0.5785E-6
METHANE (moles) 0.09700E-6

RUN # 161

TEMP(K) 559.0 TIME(s) 1000.2

MPDA (mol/L) 0.00001858 PROPENE : DIAZENE 85.2 : 1

NITROGEN (moles) 0.4978E-6
METHANE (moles) 0.08649E-6

RUN # 162

TEMP(K) 559.0 TIME(s) 1000.2

MPDA (mol/L) 0.00001589 PROPENE : DIAZENE 85.2 : 1

NITROGEN (moles) 0.4385E-6
METHANE (moles) 0.06584E-6

RUN # 164

TEMP(K) 559.0 TIME(s) 1000.2

MPDA (mol/L) 0.0002306 PROPENE : DIAZENE 9 : 1

NITROGEN (moles) 5.155E-6
METHANE (moles) 1.064E-6

RUN # 165

TEMP(K) 559.0 TIME(s) 1000.2

MPDA (mol/L) 0.0001942 PROPENE : DIAZENE 9 : 1

NITROGEN (moles) 4.295E-6
METHANE (moles) 0.9850E-6

RUN # 166

TEMP(K) 559.0 TIME(s) 1000.2

MPDA (mol/L) 0.0001684 PROPENE : DIAZENE 9 : 1

NITROGEN (moles) 3.803E-6
METHANE (moles) 0.7748E-6

RUN # 167

TEMP(K) 559.0 TIME(s) 1000.2

MPDA (mol/L) 0.0001448 PROPENE : DIAZENE 9 : 1

NITROGEN (moles) 3.265E-6
METHANE (moles) 0.6781E-6

RUN # 168

TEMP(K) 559.0 TIME(s) 1000.1

MPDA (mol/L) 0.0001128 PROPENE : DIAZENE 9 : 1

NITROGEN (moles) 2.570E-6
METHANE (moles) 0.5754E-6

RUN # 169

TEMP(K) 559.0 TIME(s) 1000.2

MPDA (mol/L) 0.00008062 PROPENE : DIAZENE 9 : 1

NITROGEN (moles) 1.812E-6
METHANE (moles) 0.4314E-6

RUN # 218

TEMP(K) 559.0 TIME(s) 725.9

MPDA (mol/L) 0.00003759 PROPENE : DIAZENE 0.992 : 1

NITROGEN (moles) 0.5419E-6
METHANE (moles) 0.1750E-6

RUN # 223

TEMP(K) 559.0 TIME(s) 736.8

MPDA (mol/L) 0.0001135 PROPENE : DIAZENE 12.00 : 1

NITROGEN (moles) 1.418E-6
METHANE (moles) 0.3710E-6

RUN # 227

TEMP(K) 559.0 TIME(s) 743.1

MPDA (mol/L) 0.0001123 PROPENE : DIAZENE 6.107 : 1

NITROGEN (moles) 1.467E-6
METHANE (moles) 0.5315E-6

RUN # 230

TEMP(K) 559.0 TIME(s) 750.3

MPDA (mol/L) 0.0001138 PROPENE : DIAZENE 1.049 : 1

NITROGEN (moles) 1.599E-6
METHANE (moles) 0.6431E-6

Appendix D†

COMMENTS ON DATA TREATMENT BY A.C. AND D.B.

YIELD *VS* TIME PLOTS

The yield *vs* time plots were questioned because the intercepts at zero time were not set at zero, as they should be if the yields are equal to zero at zero time. In fact the plots are least squares linear fits to the data which were designed to determine the presence or absence of intercepts. In particular a negative intercept on the yield axis would indicate the presence of an induction period. It was also pointed out that the rate of product formation need not be constant over the yield time periods and that plots of yield divided by time *vs* time should be extrapolated to zero time in order to obtain the rate at the beginning of the reaction. These points will be discussed with respect to yield *vs* time data at 529.4 K and at 559.0 K as reported in Tables 2 and 3.

Data at 529.4 K

These data are extremely smooth and seem to provide answers to the questions which were raised.

1. The plot of moles of nitrogen *vs* time appears to be quite linear with an intercept close to the origin. Unweighted least squares fitting gives these results, for both linear and quadratic equations.

	INTERCEPT	SUM OF SQUARES OF YIELD RESIDUALS
LINEAR	$(-3.06 \pm 7.67) \times 10^{-8}$	1.08×10^{-13}
QUADRATIC	$(-1.13 \pm 1.42) \times 10^{-7}$	9.98×10^{-14}

Intercepts are small, errors are larger than the intercepts, and a quadratic

† Added after receipt of referee's comments.

equation is not favoured over a linear equation.

2. The plot of yield of nitrogen divided by time *vs* time is shown in the figure. The intercept at zero time is $(2.97 \pm 0.15) \times 10^{-10}$. If the mean of all yields, in this set of data, divided time is calculated the result is $(3.05 \pm 0.24) \times 10^{-10}$. These are indistinguishable, indicating that the rate at any time within this time period is as valid, as an initial rate, as is the rate extrapolated to zero time.

Data at 559.0 K

1. Unfortunately the yields at 559.0 K have an inherent (that is, not due to analysis) scatter which is obvious in Figure 7. In addition, because of the speed of the reaction, data near zero time are difficult to obtain. However, the same treatment was given, with these results.

	INTERCEPT	SUM OF SQUARES OF YIELD RESIDUALS
LINEAR	$(5.54 \pm 4.62) \times 10^{-7}$	2.68×10^{-12}
QUADRATIC	$(-2.20 \pm 2.33) \times 10^{-6}$	2.44×10^{-12}

The presence of an intercept is questionable and there is little to choose between the equations. (However, the quadratic equation does not seem to be realistic because it is concave toward the time axis due to an effort to fit two or three rather fast reactions.)

2. The intercept of the yield of nitrogen divided by time *vs* time is $(3.99 \pm 0.49) \times 10^{-9}$ and the mean of yields, in this set of data, divided by time is $(3.51 \pm 0.43) \times 10^{-9}$. It is possible to conclude that the rate is slightly faster initially than it is later. However, the extrapolation to zero time is long and seems strongly biased by the two or three fast reactions. The assumption was made that all rates over the early time period were equally valid as initial rates.

Perhaps more data at 559.0 K could be obtained, especially at shorter time periods.

Order

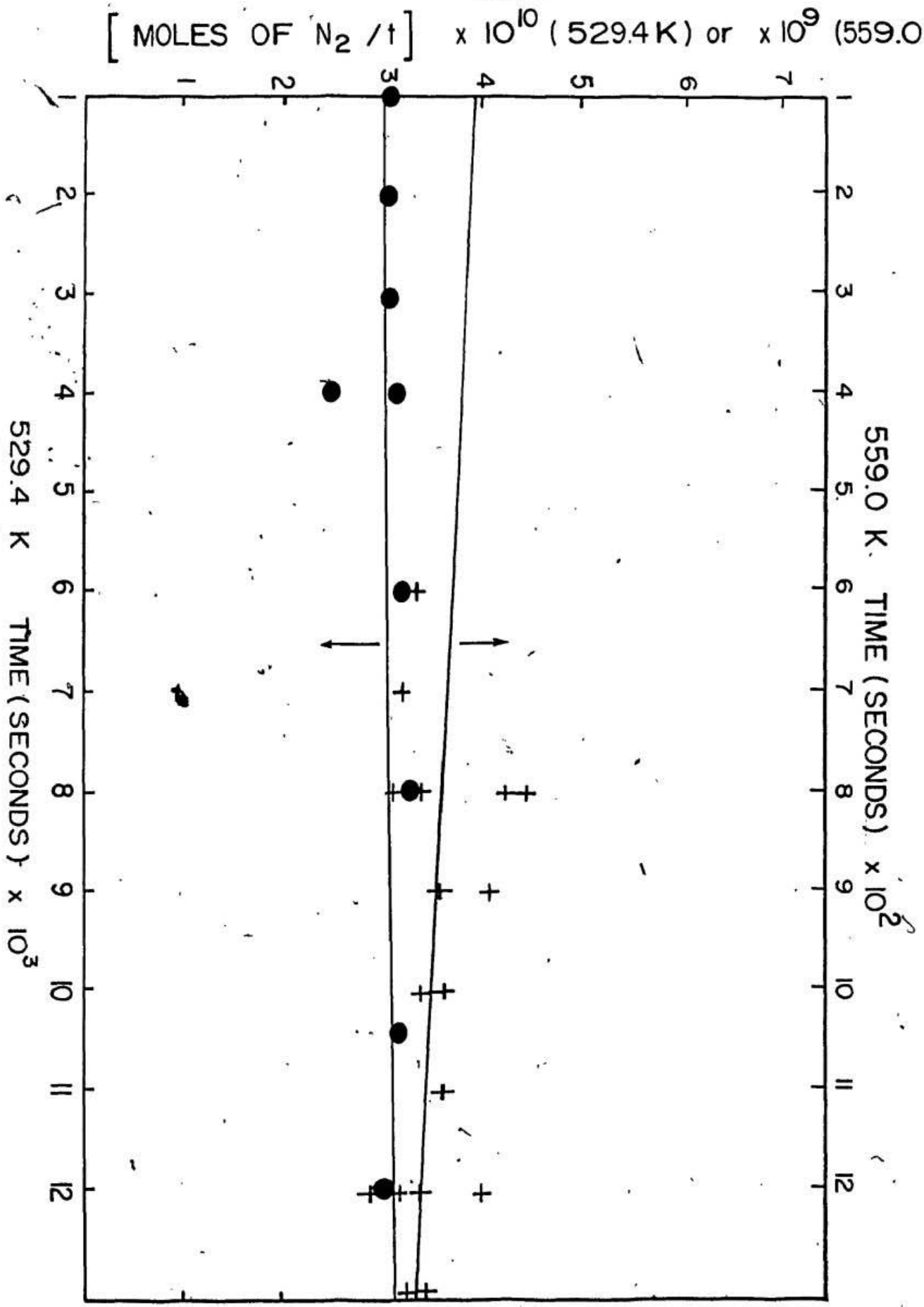
An additional comment on order may be useful. The order for nitrogen at 529.4 K is 0.99 ± 0.07 and at 559.0 K is 1.07 ± 0.03. In order to treat temperature dependence, rate constants have to have the same units, so an order has to be selected. Although the mean order is 1.03 ± 0.04 the decision was made to calculate first order rate constants. These may have the advantage of easy comparison with literature values, which are often reported as first order rate constants.

Summary

1. The rates throughout the initial period (for example 1200 s at 559.0 K and 12,000 s at 529.4 K) were treated as the initial rates.

2. Rate constants were defined by this equation

$$k = \frac{\dfrac{\text{moles of } N_2/\text{volume}}{\text{time}}}{\text{initial concentration of diazene}} \text{ seconds}^{-1}.$$


[MOLES OF N_2 /t] x 10^{10} (529.4 K) or x 10^{9} (559.0 K)
1 2 3 4 5 6 7
529.4 K TIME (SECONDS) x 10^{3}
559.0 K TIME (SECONDS) x 10^{2}
1 2 3 4 5 6 7 8 9 10 11 12